Forensic Engineering: Part B.

Four Classes of Metallurgical and Mechanical Failures

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Introduction –

This is Part B. of a two-part course on forensic engineering that considers the analysis of metallic material failures. Part A. presented an introduction to forensic engineering and the steps in completing root-cause failure analyses (RCFA). Part B. discusses important specific mechanisms of metal failure and provides alternative control methods for each that may be used to prevent a reoccurrence. Among the failure mechanisms reviewed, the several forms of aqueous corrosion are given special attention.

Specific Metallic Materials Failure Mechanisms –

There is a wide range of potential ways that metallic materials and thus parts and components in various types of equipment and facilities can fail but a smaller list accounts for most. These are as follows:

- Static stress overload
- Cyclic stress overload, i.e., mechanical fatigue
- Various forms of corrosion
- Various forms of wear

Static stress overload –

Typically this is the final stage of a failure that was initiated by another mechanism. Examples include the final stage of a failure that started by fatigue or by a corrosion process after which there is insufficient material remaining to withstand the applied service loads. Less common is stress overload failure caused by conditions that were not anticipated. These might include a service loading that imparts a different form of stress that was not accounted for in the initial design, undetected stress concentration points that were created during the manufacturing process, material mix-up so that a lower strength alloy was mistakenly installed or operation at higher temperatures than planned so that the metal's strength at that temperature is inadequate.

Failure by this mode can also take place without a fracture when the applied static stress exceeds the yield strength of the material and unacceptable plastic deformation occurs. That situation may constitute a failure when even a small amount of permanent dimensional change cannot be

tolerated in the given application. This occurs in ductile materials when significant plastic deformation takes place but the ultimate strength is not exceeded.

Although not very specific, perhaps the most practical control measure to prevent failure by static stress overload is to carefully consider during the design phase if the chosen material is likely to fail by *other* mechanisms, i.e., fatigue, or one of the various forms of corrosion or wear, in the given application. Taking actions to minimize the beginning of a failure process by one of these other methods is the best way to assure that stress overload will not appear as the final step.

Other corrective actions for resisting failure by this mode may include a variety of measures depending on the specific application. These could include changing the design but using the existing material, changing to a new material, changing the safety factor applied or, as in all failure mechanisms, making some basic modification to the service conditions. Some specific considerations regarding the design and material used might include the following:

- Research all service conditions, particularly the viable worst-case situations, to assure that maximum stresses and temperatures to which the material will be subjected have been defined and incorporated into the design.

- Consider the possible types of stresses the material will experience in service and make provisions through the selected material, dimensions and safety factor to handle them. For example the applied stress forms might be tension, compression, shear, bending, torsion or, frequently, a combination of these. Residual stresses that cannot be relieved after welding or cold working can have a major effect on failure and should always be considered.

- Eliminate all possible stress concentration points. Some of these might include small radii, sharp corners, weld beads that cannot be ground smooth or machined holes and slots. It may be that some of these must remain so the designer has to be aware they exist and apply stress concentration factors to account for the resulting, raised local stresses.

- Determine whether or not any plastic deformation of the material is permissible in the given application. If not, then choose a material with appropriate yield strength.

- If very low service temperatures are expected choose a material with sufficient fracture toughness at that temperature to prevent brittle fracture.

Mechanical fatigue –

It has been estimated that 80 to 90% of all failures of materials that are mechanical in origin are due to fatigue. This is because there are so many applications in which cyclic or fluctuating stresses exist. Such stresses can be produced by vibrations, e.g., due to irregular air movement and other forces on an aircraft's structure, and by the many irregular forces encountered in applications in which rotating and reciprocating parts are used. Thermal fatigue occurs in metal subjected to reoccurring, large changes in temperature that cause movement due to expansion and contraction of the material. Surface or rolling fatigue refers to fatigue generated by shearing stresses that are created in the many situations where there is rolling contact between surfaces.

Fatigue failures initiate, generally on the surface of the metal, as a crack that then propagates over time through the metal's thickness until there is not enough material left to withstand the applied load. The stress level necessary to initiate a fatigue crack - with cyclic stresses acting – is usually well below the stress level required to cause static stress failure. Tensile stresses are necessary to advance a growing crack while compressive stresses retard crack growth.

The appearances of fatigue-fractured surfaces frequently are distinctive at both the macro and micro-scale levels. On a macro-scale the cyclic nature of the impressed load results in a pattern of ridges across the metal surface that are known as beach marks. The marks are so named because they resemble a pattern of ridges left in beach sand by the action of receding water. Another feature of fatigue is there is little or no clear plastic deformation of the metal and thus failures have the appearance of brittle fractures.

At the microscopic level – as seen in a scanning electron microscope (SEM) – a fatigue-fractured surface often shows a series of very small ridges known as striations. Striations are oriented perpendicular to the direction of fatigue crack growth. Each striation is produced by a cycle of stress and observation of these features always indicates that fatigue has occurred. However, the absence of detectable striations does not mean that fatigue has not taken place. This latter situation can occur due to the mechanical properties of the material being examined or because service debris or corrosion products obscure the striations generated during crack propagation.

Fatigue is classified as either low-cycle or high-cycle according to the number of cycles of stress that occur before failure. Low-cycle fatigue is generally defined as just a few hundred cycles up to approximately 10,000. The high-cycle mode usually entails at least 50,000 and typically many more cycles. Comparatively low service stresses in the elastic range of the material occur in-high-cycle fatigue producing relatively long service before failure. Higher stresses and especially strains in the plastic range apply to low-cycle fatigue and much shorter service lives result. Extensive study has been done on all aspects of fatigue – but still much is unknown. This is especially true for low-cycle fatigue.

Fatigue failures include three parts – crack initiation, crack growth (or propagation) and final fracture. The latter is by stress overload and, relative to the first two, it occurs very rapidly. The major portions of the total fatigue of the material in a given application are consumed by crack initiation and propagation. Within a given a high-cycle fatigue application, the crack initiation portion of the total fatigue life is longer than the crack propagation period. By contrast, the higher stresses in low-cycle fatigue mean that crack initiation occurs quicker so that this part of the total life is shorter than the time of crack propagation. Analysis and predictions of total life in a given application of low-cycle fatigue are more difficult than the simpler situation in the high-cycle mode. One reason is that some materials develop increased strength when they are plastically strained (strain hardening) and others become weaker when plastically deformed.

Fatigue typically initiates on the surface of a metal at some type of stress concentration feature. These features may be geometric such as at a hole, at a keyway, at a sharp radius on a step change in diameter on a shaft or at a notch on the stressed component. Stress concentration points also often are caused by less distinct surface features such as stamped identification marks, grinding scratches and machining marks. In addition, fatigue cracks can start at subsurface metallurgical abnormalities such as inclusions or porosity.

Knowledge of alternative ways to design for longer service lives for equipment subject to fatigue failures are useful in analyzing why those failures occur. Three basic design approaches have been employed. Each of these methods will be briefly described.

The earliest method used applies to high-cycle fatigue. The general approach is to establish a design stress level that is sufficiently low so that fatigue cracks never initiate. The procedure employs experimentally generated curves of applied stress (S) versus logarithms of the number
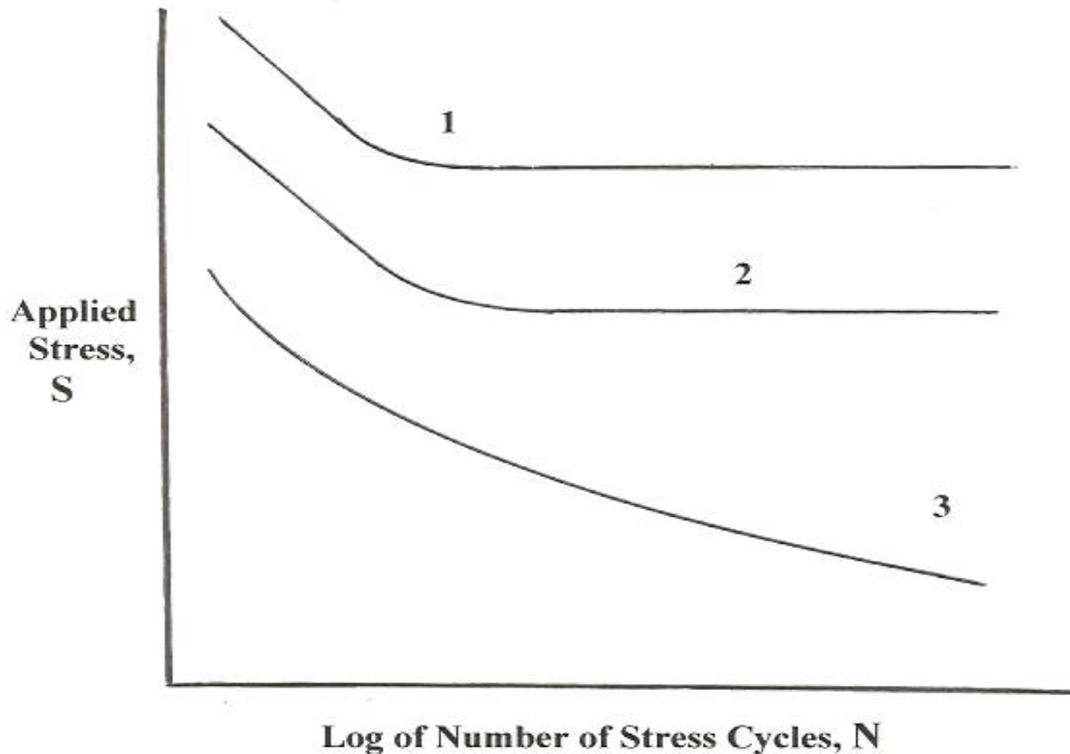
(N) of cycles to failure at a given stress level for the material in question. Three such curves are shown schematically in Figure 1. Multiple data points have been omitted for clarity.

Figure 1. – Schematic Representation of Experimentally Determined S-N Data

Horizontal sections of curves 1 & 2 define the endurance limits, i.e., the fatigue strengths, of these alloys for the conditions used in the tests.

Curves 1 and 2 apply to ferrous alloys and to titanium alloys in non-corrosive test conditions. The alloy represented by Curve 1 has a higher endurance limit compared to the material represented by Curve 2.

Curve 3 represents either an aluminum or a copper-based alloy because those classes of alloys never have endurance limits. Curve 3 also is applicable to a ferrous or to a titanium alloy that was exposed to corrosive conditions, i.e., corrosion fatigue was active when the data were generated and thus no endurance limits are displayed.

The designer seeks to assure that the actual service stress on the part or component being designed is maintained below the S versus N line through plotted data points for the desired number of cycles. Stresses are assumed to remain in the elastic range of materials evaluated. Steels as well as titanium alloys when fatigue tested in a benign, non-corrosive environment typically will provide test data that results in a horizontal section in their S-N curves. This horizontal portion – shown in Figure 1 – defines what is known as the endurance limit or fatigue strength of the particular material for the specific conditions used in the test. This simplifies design because it has been shown that as long as the service stress is kept below the endurance limit for the given material then essentially an infinite number of stress cycles can be sustained without failure.

It should be understood that actual fatigue service conditions likely will differ from the laboratory conditions used to generate S-N data for a given material. Factors such type of stress loading, presence of a mean stress in the tensile range, size and shape of test specimens, presence of stress risers, surface condition of test specimens, testing temperature and the corrosiveness of the test environment all can have significant effects. For example, even moist air can constitute a corrosive condition that will affect fatigue life. Each of these variables will generally act to produce failure at a lower number of stress cycles in service compared to the lab results. The endurance limit of a given steel in service will likely be lower than its value as defined in laboratory testing. The designer will generally recognize these effects and account for them by applying adjustment factors to the laboratory data plus apply an additional safety factor to account for unknowns. The failure analyst needs to understand the need for these adjustments and determine whether or not they were reasonably addressed in each failure situation.

As shown in Figure 1, non-ferrous alloys such as aluminum and copper-based alloys do not produce a horizontal portion in their plotted S-N data and thus they have no endurance limits. Also, materials that have a clearly defined endurance limit in a benign service environment lose this behavior when exposed under the same mechanical conditions in a corrosive environment. This is corrosion fatigue – a combination of mechanical fatigue and corrosion. For alloys or service conditions that produce no endurance limit, stress levels must be restrained to low values if longer life and many cycles are needed for the application.

S-N data generation for proper use in design is not a simple process. Scatter in the data generated is always an issue. Statistical methods are used to rationally address experimental variations.

The second basic design and analysis method for fatigue applies to low-cycle situations. Here the procedure is to experimentally generate plots of strain data versus number of strain cycles at which failure occurs for the material in question. As in the high-cycle design approach, the assumption with low-cycle fatigue design is that the design parameter, i.e., strain in this case, is limited so that a fatigue crack is never initiated. A basic difference here compared to the S-N method is that plastic deformation of test specimens *does* occur in low-cycle service. Also, generation of the experiment data as a basis for good design is more difficult and results are more uncertain as compared to the S-N, high-cycle method.

Data produced by the strain-versus-cycles-to-failure approach are often applied in designing for cyclic strains caused by expansion and contraction of metals at high temperatures where there is at least partial restraint of movement. This is thermal fatigue. It may occur in applications such as steam boilers, nuclear power plants and chemical reactor vessels. There are clear similarities between mechanically induced, low-cycle fatigue (used to generate strain versus N data) and the effects produced by thermal fatigue. However, the high temperatures associated with thermal fatigue can have the extraneous effect of changing fundamental material properties that do not occur in mechanically produced low-cycle fatigue at lower temperatures. Thus the failure analyst has to be careful in attempting to apply mechanically produced strain versus N data (generated at ambient temperature) to situations involving thermal fatigue.

The third method of fatigue analysis and design uses principles from fracture mechanics. It has been used extensively in the aircraft and aerospace industries. The procedure is known as the damage-tolerant approach because, unlike the S-N and strain versus N methods, a fatigue crack is assumed to exist *initially*. Techniques are used to determine: (1) the critical, final size of the crack at which time final fracture (called fast fracture) and failure will occur and/or (2) the time period, i.e., number of cycles, required for the crack to propagate from its initial to its critical size. Non-destructive evaluation (NDE) techniques are used in conjunction with fracture mechanics predictions to implement a planned monitoring and inspection program.

There are several engineering alloys that have sufficient values of fracture toughness for various applications. This property indicates their resistance to crack enlargement. In higher toughness alloys crack growth is relatively slow. Service temperature is a key factor in a material's fracture toughness with lowest toughness values occurring at low temperatures. In common fatigue-loading situations with a suitably tough alloy, the rate of growth of a crack prior to final, fast fracture is slow enough so that crack enlargement can be assessed by planned, periodic NDE

measurements. Corrective action can then be taken before a crack reaches its critical size. Fracture mechanics theory provides the basis for predicting critical crack size when the material's fracture toughness is known or assumed.

Effective predictions of critical crack size and thus time to final failure for a given initial crack size depend on several parameters apart from the given material's fracture toughness. Included are the nature of the stress distribution at the crack tip; the thickness and type of loading on the component being evaluated; the nominal static, applied stress on the component and the peak as well as low amplitude fluctuating loads possible in the particular fatigue service. Clearly, the designer and the individual planning the NDE program need to be well informed about the several factors involved with this methodology. However, with needed knowledge and experience this approach offers many advantages and is successfully used.

Following are several actions available for potential use to control fatigue failures:

- Eliminate or minimize all possible surface stress concentration points. Geometric stress risers include fine threads in fasteners, sharp corners in keyways and elsewhere, lack of penetration and/or undercut areas in welds and gas porosity voids that extend to the surface of cast materials. Surface finish features that create stress risers might include mill scale, burrs, machining and grinding marks.

- If the service atmosphere is even slightly corrosive and the material being used has marginal corrosion resistance small pits may form and these are common locations for fatigue crack initiation. Choose an alloy that has sufficient corrosion resistance for the service environment.

- Input compressive stresses to the material surface via shot peening, tumbling of small parts or cold rolling of plate material using hardened rolls. Proper case hardening to the surface by carburizing or nitriding processes is often used to leave beneficial compressive stresses on the surface.

- Avoid harmful tensile stresses on the surface caused by electroplating processes.

- Minimize operational tensile stresses, i.e., the mean stress applied. This is defined as one half of the algebraic sum of the maximum and the minimum fluctuating service stresses.

- Avoid service stress loading in a transverse direction, i.e., stress that is perpendicular to elongated grains formed in a material by rolling or forging processes. Alloys processed this way are weaker in the transverse direction.

- Apply one of the three alternative approaches to fatigue design after implementing applicable actions from the above list.

Corrosion –

Other than fatigue, the several forms of aqueous corrosion represent the most common class of metallic material failures. Corrosion typically is found in or on a wide variety of equipment and facilities including structural steel; automotive vehicle body parts; above or below ground tanks and pressure vessels; aircraft; marine vessels and pier structures; various types of heat exchangers; above and below ground piping plus many other applications. Corrosion exists in one form or another in almost every industry.

Aqueous corrosion is an electrochemical process and two kinds of reactions always occur. One reaction is an oxidation process in which electrically neutral metal atoms are converted into electrically charged ions of that metal as free electrons are released. Oxidation occurs on the anodic areas of the attacked material. There is only one type of anodic or oxidation reaction. Simultaneously a reduction electrochemical reaction occurs in which electrons are consumed. This occurs on the cathodic areas of the attacked metal. Unlike the single oxidation reaction, there are several possible types of reduction or cathodic reactions. Some very common cathodic reactions are the reduction of oxygen (in neutral or basic pH solutions) to hydroxide ions, the reduction of oxygen to water (in acidic solutions) and the reduction of hydrogen ions (in several types of solutions) to gaseous hydrogen that is given off. The solution in which the anodic and cathodic reactions occur is the electrolyte. This is the essential corrosive medium that conducts the electric current generated during the corrosion process.

Thermodynamic laws dictate that corrosion *will* occur for most practical combinations of engineering alloys and electrolytes unless there is intervention to modify the naturally occurring process. The important question is what will be the speed or kinetics of the corrosion reactions. A basic law of electrochemistry of corrosion is that the oxidation and the reduction reactions must proceed at the same rate. If the kinetics of one of these reactions is decreased an equivalent

rate decrease will occur in the other reaction. Corrosion-control methods are based on the concept of decreasing the rate of one or both of the electrochemical reactions and thereby reducing the speed of the overall corrosion process to practical levels.

There are general application factors that affect the incidence and kinetics of most aqueous corrosion processes. *Service temperature* has a major affect - each 18 degree F (10 degree C) increase in temperature will generally double the rate of corrosion. *Heterogeneous conditions* favor the incidence and rate of corrosion. Some examples include galvanic corrosion that occurs when dissimilar metals are in contact; greater attack on an alloy of a metal compared to lower rates on a pure metal; greater attack at the unordered and mixed conditions of the grain boundaries of a metal compared to the ordered crystalline structures within grains and greater attack at areas on a metal that are exposed to high levels of applied or residual stress compared to nearby areas that are not. *Electrolyte velocity* relative to the exposed metal surface is a unique and often critical factor. Low velocities and stagnant conditions accelerate some forms of corrosion while, ironically, such conditions minimize attack by other forms.

There are **four primary methods of corrosion control** in wide usage that may be applicable for a given service or corrosion mechanism. These are as follows:

Provide a coating – this is probably the most widely used method of control. In the typical case the coating provides a barrier between the susceptible metal and the electrolyte. Some of the types of coatings are electroplating, galvanizing or using a primer plus topcoat of paint. In the case of galvanizing on steel, the zinc has two functions. First it provides a barrier and, secondly because it is a more "active" metal, i.e., more likely to corrode than the steel substrate, it also preferentially corrodes and in the process protects the steel from corroding. The latter function is an example of another method of corrosion control – cathodic protection.

Organic and inorganic paint systems consisting of a primer and a topcoat are the most common form of coatings used. The most important factor in making them effective is the surface preparation used. This is essential to obtain adherence to the substrate metal. Carbon steel is the metal most commonly painted for corrosion control. Other metals such as stainless steels and nickel alloys are not painted because they have the capability to form a very effective protective surface film – a passive film – whereas this capability in carbon steel is, by comparison, much inferior.

Provide cathodic protection – there are two forms of this method but on a micro-scale both are very similar. Corrosion involves a flow of electric current from the corroding metallic surface. Both types of cathodic protection (CP) function by supplying a current onto the exposed and susceptible metal. This counter flow doesn't stop the corrosion process but it reduces it to practical rates. The two types of CP are sacrificial anode and impressed current. In the former a metal that is very active or anodic in a galvanic series is electrically connected to a more noble or cathodic metal and a galvanic couple is established. The more active metal then preferentially corrodes and "sacrifices" itself so that in the process the more noble metal is protected. In the case of impressed current CP a rectifier/transformer is used to decrease incoming AC electrical voltage and change the AC to DC (corrosion current is DC) that is in turn fed to the metal surface being protected. Both forms of CP have advantages and disadvantages.

An organic coating is typically used along with CP because the resulting current required from the CP system to achieve protection is greatly reduced. CP is frequently used for corrosion control on underground structures such as pipelines and tanks but it is also used for the hulls of ships and on the inside surface of above ground tanks that store corrosive liquids.

Select an appropriate material – this control method entails specification and use of a material that inherently provides practical corrosion resistance for the particular electrolyte and other service conditions in the application. Of course corrosion resistance is just one of the several criteria that usually have to be considered in selecting a suitable engineering material.

So far as the corrosion resistance requirement, the analyst needs knowledge of what combinations of alloy and electrolyte work well together and which do not. For instance, stainless steels that have a high level of molybdenum (Mo) as an alloying element provide good levels of resistance to pitting and crevice attack in electrolytes that have high levels of chloride ions - as in brackish water and seawater. However, Type 316 stainless steel that contains Mo provides inferior resistance to corrosion by nitric acid as compared to Type 304 stainless that has no molybdenum.

Less obvious material choices should also be considered. These might include polymers or composite materials that don't fail by electrochemical corrosion. These corrosion-resistant non-metals may be useful if they can satisfy other necessary criteria such as providing resistance to high temperature or having sufficient strength. Another option might be to weld or metallurgically bond a thin top layer of an expensive alloy for corrosion resistance to a much

thicker substrate of plain carbon steel that provides the mechanical strength needed for the given application. This combination can provide strength, corrosion resistance and low cost.

Select a chemical corrosion inhibitor – this control method involves both the specification and correct usage of a trace chemical that is added to the electrolyte to interfere with the corrosion process. An effective inhibitor may affect the oxidation reaction, the reduction reaction or both to lower the overall rate of corrosion. The inhibitor is selected for the specific electrolyte and metal to be protected. A common example is the addition of an inhibitor that reacts with residual oxygen in boiler feed water in a steam boiler and chemically deactivates it to prevent oxygen pitting corrosion at the downstream, high operating temperatures. This is an oxygen scavenger.

Inhibitors are most frequently used in water circulating systems. Applying the correct dosage (in parts per million), using the correct method and frequency of inhibitor injection and performing consistent monitoring of effectiveness are essential to success. The individual recommending the inhibitor for a specific application needs a thorough knowledge of the metallurgy & electrochemistry of the system plus the facts about any negative effects that might occur with alternative combinations of particular inhibitors and concentrations.

Overview of important corrosion mechanisms and their control –

Figure 2 provides schematic sketches of the comparative, physical characteristics of some of the forms of aqueous corrosion.

Specific information follows on each of the more important forms of corrosion and some alternative ways to control each:

General attack – This involves uniform penetration and material loss on susceptible metal surfaces exposed to aggressive electrolytes. At different times during the corrosion process anodic and cathodic areas change their locations. The rate of attack may be slow or rapid but since the process occurs in a relatively uniform manner damage is less threatening and periodic monitoring is effective and simpler compared to the many localized forms of corrosion.
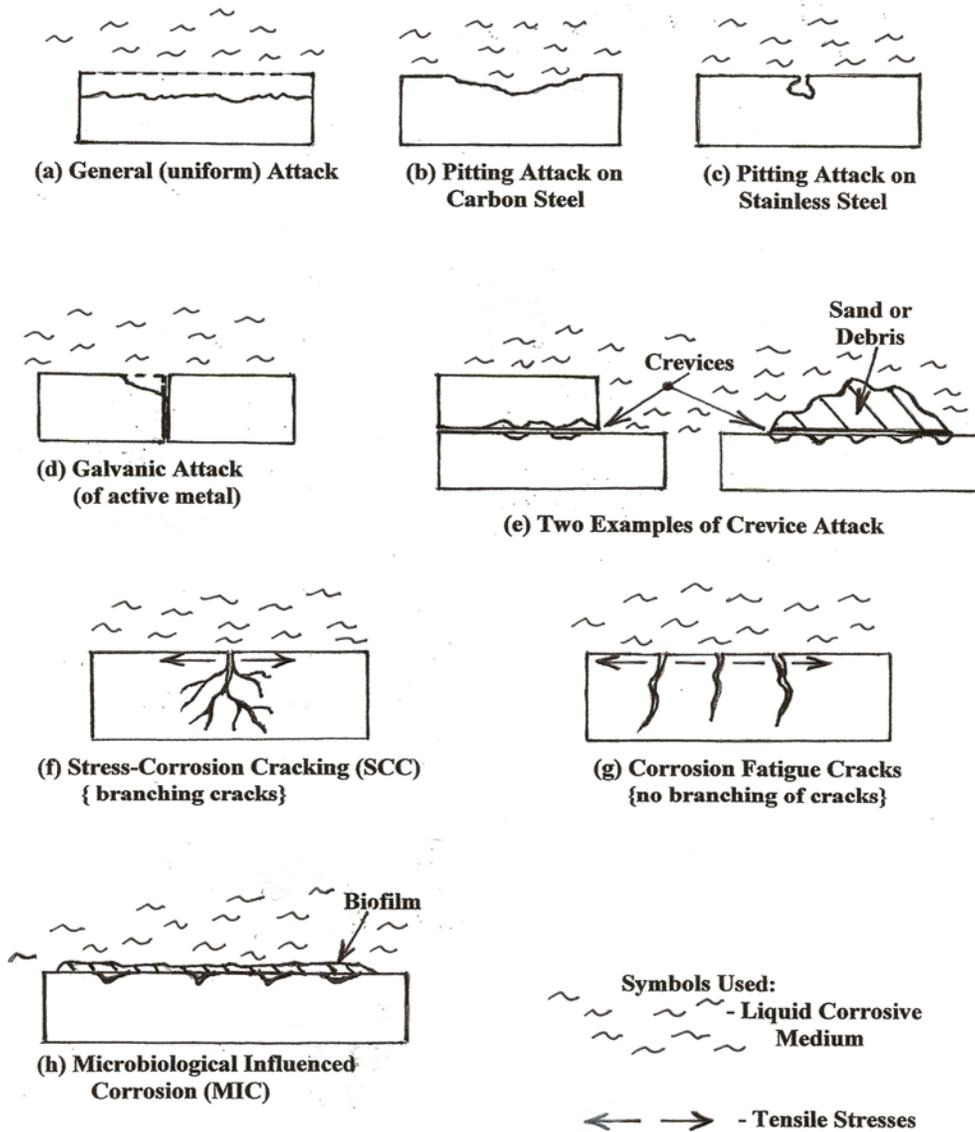
Corrective or preventative actions for general corrosion can include the following:

Use a material that is inherently resistant to the electrolyte and service conditions.

Figure 2. – Schematic Cross Sections of Metal Exposed to Some Common Forms of Aqueous Corrosion

(a) General (uniform) Attack

(b) Pitting Attack on Carbon Steel

(c) Pitting Attack on Stainless Steel

(d) Galvanic Attack (of active metal)

(e) Two Examples of Crevice Attack

(f) Stress-Corrosion Cracking (SCC) { branching cracks}

(g) Corrosion Fatigue Cracks {no branching of cracks}

(h) Microbiological Influenced Corrosion (MIC)

Symbols Used:
∼ ∼ ∼ - Liquid Corrosive Medium

← → - Tensile Stresses

Implement a regular monitoring and replacement program, i.e., make regular, planned ultrasonic NDE thickness measurements and replace exposed metal as needed prior to failure.

Use a coating - either alone or in conjunction with CP.

Determine the mechanical strength, along with a safety factor allowance, to define the minimum thickness of a metal to meet its applied stress criterion and then add extra thickness as a "corrosion allowance". This is often done in the design of pressure vessels and tanks and can be very effective when combined with regular thickness monitoring by NDE. However, it is important when using this approach to be confident that a more rapid, localized form of corrosion that is more difficult to monitor will not occur. Localized forms include, for example, pitting or stress-corrosion cracking.

Correctly use an appropriate corrosion inhibitor when the application permits.

Galvanic corrosion – This form involves two or more dissimilar metals that are in electrical contact while each is exposed to an aggressive electrolyte. A classic dangerous galvanic coupling of metals is mild steel and copper (or brass) in water. The metal that offers more resistance to the given electrolyte is said to be the noble or cathodic metal in the galvanic couple while the other metal, with less resistance is said to be the active or anodic member. In galvanic corrosion the most active metal corrodes at a much faster rate than it would if exposed alone in that same electrolyte. However, the noble metal corrodes at a slower rate than if exposed by itself. Depending on the conductivity of the electrolyte, the attack of the active metal is generally greatest closest to its interface with the noble metal.

Many engineers are familiar with using a standard galvanic series, i.e., an ordered listing of different alloys and metals according to a measured property for each, i.e., its electrochemical corrosion potential, when exposed to seawater. The traditional use of this series is to avoid galvanically coupling metals that are far apart in the series while implicitly assuming that it is acceptable to couple metals that are very close together in the series. This approach can provide general guidance in many applications but it has limitations. First corrosion potentials are thermodynamic parameters and a standard galvanic series provides no information on the possible important kinetic interactions between alloys. Secondly, a standard galvanic series is developed with seawater. Other electrolytes can produce a different ordering of corrosion

potentials for the same metals. Finally, some metals change their positions in a standard galvanic series relative to other metals when certain temperature levels are exceeded. Measurements for a standard galvanic series are done at or near ambient temperature and do not account for this effect.

Corrective or preventative actions for galvanic attack can include the following:

If possible, avoid dissimilar metal galvanic couples entirely.

If a potential galvanic couple is unavoidable – separate the metals with an electrical insulating material. Also, the relative areas of the anodic (active) and the cathodic (noble) metals in unavoidable electrical contact are important to the rate of galvanic corrosion that occurs. Avoid a small anodic metal area directly coupled to a large cathodic metal area. For example, given the choice, it is much better to have copper or brass fasteners in a large-area steel plate than to have steel fasteners in a large-area copper sheet. Copper (or brass) is the noble metal and steel is the active metal in both of these couplings but the anode-to-cathode area ratios are very different.

Coatings always have very small-area defects known in the painting trades as "holidays" where the substrate metal is not covered. Therefore, if a partial coating is used to control this mechanism, coat the cathodic (noble) metal in the couple and not the anodic metal. This will upset the electrical contact between the two metals and thus control galvanic attack. If only the anodic metal is coated the coating will have holidays and create small areas of exposed metal so that a very unfavorable anode-to-cathode area ratio is created. Coating both metals is still better.

If all other options fail, use the standard galvanic series and choose metals that are close together in the series that must be in electrical contact. However, realize the limitations of this method.

Pitting corrosion – This very common form of attack occurs at separated spots where there is a local breakdown in the naturally occurring protective layer – passive film – found on the surfaces of many metals. The stability of most passive films depends on several factors but it is least robust in plain carbon steels and most robust in highly alloyed materials such as stainless steels and nickel alloys.

Generally, the higher the alloy content in a material, the more protective is the passive film. When there is complete breakdown in a metal's passive film general corrosion occurs. This

typically is found when the given electrolyte is very aggressive or the metal has an inherently weak passive film or both. Carbon steel frequently suffers general corrosion because its passive film is unstable in a variety of corrosives. However, carbon steel can also experience pitting but it is much less susceptible than alloys that form more stable passive films.

Stainless steels most often experience pitting when specific, aggressive ions in the electrolyte breakdown their protective films at distinct, localized spots. The shape or morphology of pits on carbon steel is typically very different from pits on materials that have a robust passive film. See the differences in Figure 2, (b) and (c). Pits typically are found predominately on the horizontal, lower surfaces of equipment exposed to corrosive media.

Once initiated by film breakdown, a pit grows at a fast rate. One reason that the process is accelerated is because the anodic (oxidation) reaction occurs in the relatively small area in the pit while the catholic (reduction) reaction occurs on the larger area immediately surrounding the pit. A galvanic cell is thus established with an unfavorable anode-to-cathode area ratio. Unlike general corrosion, the anodic areas and cathodic areas on the metal surface do not change positions with time. Instead the metal penetration process continues – as long as the aggressive medium is present - in the same initial pits and thus metal loss is concentrated at these locations. For this reason pitting is much more dangerous compared to general corrosion. In addition because the pits occur at distinct spots they cannot be as easily detected and monitored compared to general corrosion. Standard metal thickness measurements by NDE taken from the external, "dry" side of a metal experiencing pitting may be a hit and miss process. Depending on the service conditions, pinhole leaks or ultimately complete rupture of pitted equipment can occur. Another problem with pits is that they often act as stress concentration sites that can be precursors to other problems such as fatigue or stress-corrosion cracking.

Specific ions in electrolytes are very effective in causing local damage to passive films on metals and thus in promoting pitting. The classic example of this is the effect of chloride ions on stainless steels. Hydrogen ions as concentrated in low pH electrolytes have a similar effect. The rate of pitting is often directly related to the concentration of chloride ions or the pH of an electrolyte. Other halide ions such as hypochlorites (as in bleach) and bromides also are harmful to the stability of passive films. Stagnant or very low flow conditions allow pitting to initiate and then grow whereas high flow conditions severely limit the initiation of pits. Stainless steel pump casings and impellers handling brackish or seawater may provide good pitting resistance as long

as the pump is in operation but pitting can occur on common grades of stainless, e.g., Types 304 or 316, when the pump sits idle and the liquid with a high concentration of chlorides remains inside.

In stainless steels the most powerful alloying elements to provide pitting resistance are molybdenum(Mo), chromium(Cr) and nitrogen(N). By contrast, small amounts of carbon and sulfur in stainless steels will lower their pitting resistance. Titanium alloys offer excellent resistance to electrolytes with high levels of chlorides present unless temperatures are very high.

Corrective or preventative actions for pitting can include the following:

Each of the four primary corrosion control methods - coatings, CP, material selection and inhibitors - can be effective depending on the specifics of the given application.

If feasible, limit the concentration of aggressive ions in the electrolyte to include avoiding low pH conditions. As always, keep the service temperature as low as possible.

Maintain a minimum flow velocity of the electrolyte at all times. Often there is no provision for *complete* drainage and pitting starts in idle equipment during shutdowns at low areas where residual electrolyte collects and concentrates aggressive ions. Careful attention to proper design details in equipment will minimize areas that cannot be fully drained.

If possible, preventative maintenance and inspection of equipment during shutdowns should always include periodic evaluations from the "wetted" side of metal surfaces. Other methods, e.g., ultrasonic metal thickness measurements, from the external side may not find the deepest pits.

Crevice corrosion – This form of attack is so named because it occurs in areas that are partially closed off from the free exchange of the electrolyte with areas just outside of the crevice. For attack to occur the required creviced area opening must be small or tight enough to prevent free interchange of the electrolyte but not so tight that the corrosive cannot enter. A variety of physical arrangements can present opportunities for crevice attack. Two of these are shown in Figure 2, (e). Other examples of sites for this type of corrosion if exposed to a corrosive medium are lapped metal plates that are tack (skip) welded rather than continuously welded; inside flanged pipe joints with an absorbent gasket material in place and under the bolt head or washer

surfaces of mechanical fasteners. It is often difficult to fabricate something without creating crevices. The designer needs to be aware of the potential harm crevices can cause in corrosive environments and take all possible actions to eliminate them. The failure analyst should look for creviced areas as possible sites for the origins of failures.

Crevice attack initiates inside the partially enclosed area so that the anodic(oxidation) process occurs there while the co-joint cathodic(reduction) corrosion reaction occurs on the area surrounding the crevice. While the initiation phases are different, the growth or propagation phases of crevice attack and pitting are almost identical. After crevice corrosion has occurred the appearance of the corroded region inside a crevice is often very similar to that of pitting.

It has been shown experimentally and in practice that for similar conditions and with the same electrolyte, crevice corrosion will initiate and start penetration into a given metal before pitting starts. Because of this fact and because of the many potential crevice sites that can occur in practice, crevice corrosion often presents more danger of a failure than pitting.

Similar to pitting, materials that form robust passive films, e.g., stainless steels and aluminum alloys, are most susceptible to crevice corrosion. Also, like pitting, carbon steel is less likely to experience crevice attack than stainless steels or aluminum. In stainless steels the alloying elements that provide the most resistance to pitting also impart the best resistance to crevice attack, i.e., Mo, Cr and N.

Corrective or preventative actions for crevice corrosion can include the following:

A very important factor is to be aware of the danger crevices can present and seek to eliminate them during the design stage of equipment. This might include providing for complete drainage and removal of all deposits that would otherwise build up inside equipment, specification of continuous and not tack (skip) welds and using non-absorbent gasket materials in piping flanges so that liquids will not be retained there.

If fabrication requirements demand that semi-closed areas remain in the finished equipment, provide for larger than minimum openings so that free interchange in & out of the electrolyte can occur. Generally this means the minimum, vertical opening dimension for the enclosed area should be approximately 0.125-inch. Collected debris can partially plug even larger openings so

it is important, if possible, to inspect and remove any debris found in these areas during maintenance shutdowns.

Wherever possible, use continuous welds and not mechanical fasteners for making joints.

If possible, minimize the concentration of aggressive ions (same ones that apply to pitting) in the electrolyte and minimize service temperatures.

If crevice attack is likely and unavoidable, stainless steel alloys that have higher percentages of molybdenum, chromium and nitrogen offer the most resistance. Aluminum alloys without copper or zinc offer the best resistance.

Environmentally induced cracking –This area of corrosion-related failure is very broad and has received more study than any other. The most commonly occurring forms are stress-corrosion cracking (SCC), hydrogen embrittlement (HE) and liquid metal induced embrittlement (LMIE). Each can cause extensive damage from a failure and preemptive detection often is difficult. Another feature is that these forms can be affected by several factors and that is another reason they have been studied so intensely.

Stress-corrosion cracking (SCC) – This mechanism includes the combination of a localized corrosion process and mechanical cracking. Three interacting factors are essential for SCC: (1) a specific, susceptible alloy, (2) a particular electrolyte, and (3) a localized applied or residual tensile stress. SCC only occurs with particular combinations of alloy and corrosive medium. Other combinations are benign so far as this mechanism. For example, when tensile stresses are present, a classic susceptible pairing that often produces cracking is copper or brass in electrolytes containing ammonia or ammonia compounds. Other potentially harmful pairings are commonly used austenite stainless steels (Types 304 or 316) or high strength aluminum alloys in electrolytes with high concentrations of chloride ions or carbon steel in sodium hydroxide (caustic) solutions at higher temperatures. By contrast, SCC is typically a very low probability with copper alloys in potable water or stainless steels in ammonia solutions or commercially pure nickel in caustic solutions.

The level of tensile stress necessary to cause SCC often is below the yield strength of the material. Sometimes is it far below – there have been situations where cracking has occurred when the tensile stress was as low as 10% of yield. This illustrates the effect of time in the

incidence of SCC. Some have claimed there is a minimum threshold stress below which cracking will not occur. However, it is more correct to conclude that a minimum stress threshold does not exist but the necessary time for final fracture to occur is greatly extended (maybe beyond practical requirements) when tensile stresses are kept very low. Another key point is that unrelieved tensile residual stresses often are responsible for more incidences of SCC than applied service stresses. Perhaps this is because residual stresses can be easy to overlook.

Other service conditions that often promote or accelerate SCC are high temperatures, physical conditions in which aggressive ions can be concentrated at particular spots on the metal and in alloys that have been sensitized to intergranular attack (IGA). All corrosion reactions typically are more rapid at higher temperatures. However, there are some combinations of susceptible alloy and specific electrolyte that will not cause SCC in a practical time period unless a given minimum temperature exists. Aggressive ions concentrate in pits and crevices and these areas are more likely to then be susceptible to SCC. As mentioned before, pits also present stress concentration sites and thus SCC cracks often originate from them. Sensitized materials (discussed later under the IGA section) are much more susceptible to cracking between the crystalline grains in the metal, i.e., producing intergranular cracking (IGSCC).

Corrective or preventative actions for SCC can include the following:

Each of the traditional four classes of corrosion control methods can be effective for SCC if practical in the particular application.

Good material selection is likely the most commonly used approach to controlling SCC. The nickel content in stainless steels and nickel-based alloys has a major effect when the electrolyte contains chloride ions. Good SCC resistance is obtained when no nickel (or less than 5%) is present as in ferritic stainless steels *and* in austenitic stainless steels or nickel-based alloys with more than about 12% nickel. However, very poor resistance occurs when the nickel content of stainless steels is between about 5 and 12 %. Common grades of austenite stainless steels, e.g., Types 304 and 316, have nickel contents between 8 and 14% and, therefore, these grades often suffer chloride-related SCC.

Avoid specific combinations of susceptible alloy and electrolyte that may be harmful. The very well known, potentially dangerous combinations were mentioned earlier. Page 831 of Reference 1 provides an extensive tabulation of alloys and media that can cause SCC.

Keep applied tensile stresses as low as possible and don't overlook the important role of residual stresses. The latter are commonly caused in certain welding applications or by cold working of metal. Use a proper stress relief heat treatment to greatly reduce residual stress levels.

Determine if beneficial compressive stresses on the surface of a susceptible metal are practical to use. This can be accomplished through shot peening or cold rolling of plate material between hardened rolls.

Avoid pitting and crevice attack in equipment. Each form of attack can provide a prelude to the start of SCC by concentrating aggressive ions, creating stress concentration areas or both.

Prevent sensitization of alloys because of their susceptibility to SCC when in that condition.

Hydrogen embrittlement (HE) - This category of failure is not a corrosion process itself because the hydrogen does not cause anodic degradation, i.e., corrosion, of the material. However, there are connections. The very small size of hydrogen atoms exposed to a susceptible metal surface allows them to diffuse in and collect primarily at the material's grain boundaries and this causes embrittlement. The atomic (nascent) hydrogen can be generated during several manufacturing processes to which the metal may be exposed. These include electroplating, acid or caustic cleaning, certain heat treatment processes and, later in service, during cathodic protection or certain corrosion processes.

The mechanical properties of hydrogen-charged materials are degraded. The changes can range from reduced ductility (more common in low strength steels that have been severely cold worked) to macro-scale brittle fracture in high strength steels. The exact mechanism of how HE takes place is uncertain.

HE most commonly occurs in high strength steels, i.e., those with ultimate tensile strengths (UTS) of 150 ksi (1034 MPa) or higher. This strength level corresponds to a Rockwell Hardness Number, C Scale of about 33 (HRC 33). Hardness of steel is directly related to its ultimate strength. Material hardness instead of UTS is commonly used as an indicator of susceptibility to HE. Even parts per million (ppm) of hydrogen can cause HE and brittle fracture in steels with hardness of HRC 40 {UTS of about 180 ksi (1240 MPa)} or more. Surface case hardening by carburizing or other processes makes a steel alloy more susceptible. HE can occur in certain nickel-based alloys if they have been cold worked to high strength levels and, also, in martensitic

and precipitation-hardened stainless steels. Certain titanium alloys can suffer HE at high temperatures, i.e., above approximately 480 degrees F (250 degrees C), when hydrogen and titanium react to form brittle titanium hydrides.

After hydrogen is charged into a high strength alloy there is no immediate fracture and, therefore, the mechanism is often referred to as a delayed failure process. Some time must elapse after hydrogen entry occurs and a sustained level of tensile stress acts before fracture occurs. This stress can be at a level below the yield strength of the alloy. The stress may be applied or, very frequently, fracture occurs due to unrelieved residual stresses left in the material due to manufacturing processes such as welding, heat treatment or assembly. Residual stress levels can be detected, as stated in Table 2 in Part A. of this course, using the X-ray diffraction (XRD) material characterization technique. Because of the presence of residual stresses, the delayed fracture result can take place after a susceptible part is manufactured but before it is put into service. This characteristic is one of the key indicators for distinguishing HE from other forms of failure. Another feature of HE is that the failed part typically shows no macro-scale plastic deformation and thus it appears to have experienced a completely brittle fracture. HE cracks, like corrosion-fatigue cracks, typically follow a single path and are not branched like SCC cracks. See Figure 2 (f) and (g).

Except for those cases of titanium hydride formation at high temperatures in titanium alloys, HE typically is most severe at ambient temperatures. Further, the tendency for cracking decreases as the temperature increases. In steels, HE is essentially eliminated at temperatures above 390 degrees F (199 degrees C).

Corrective or preventative actions for hydrogen embrittlement can include the following:

It is essential to distinguish the different roles of cathodic protection (CP) in relation to SCC compared to HE. CP is generally helpful in controlling the anodic corrosion that is a major component of the SCC mechanism. However, CP can be the cause of HE in certain applications. This occurs when a damaging cathodic applied potential, i.e., a very negative voltage, is used and atomic hydrogen is generated (by breaking water into its hydrogen and oxygen parts) so that hydrogen can be charged into a HE-susceptible alloy.

Proper steel selection is likely the most effective control measure for HE. Use *lower* hardness and strength materials whenever possible. As general guidelines, limit the final specified

hardness (after all corrective processing) to a maximum hardness of HRC 40 or less and limit the material's UTS to 180 ksi or less. In low strength steels, minimize the extent of cold working to minimize loss of ductility when exposed to nascent hydrogen

Specify an appropriate post-processing corrective action after each manufacturing step that can increase hardness or leave residual stresses in the material. This should include tempering after hardening heat treatment and stress relieving after severe cold working or welding of susceptible alloys.

Assure that electroplating process parameters are carefully controlled to limit hydrogen entry into the plated metal during plating and maximize its exit by a sufficient bake-out period after plating. Regarding the latter, Reference 1, page 822, makes the point that the bake-out procedure needs to be done within one hour after plating is completed to be most effective.

Carefully control the parameters used during the acid cleaning of metals. Included is the acid concentration and temperature used, the time in the acid bath and the methods used to achieve complete drainage of cleaned metal after the process.

Liquid metal induced embrittlement (LMIE) and solid metal induced embrittlement (SMIE) - These mechanisms of failure are much less common compared to SCC or HE but they do occur in special situations. LMIE occurs much more often in service than SMIE. It is necessary for a specific combination of susceptible alloy and a specific embrittling metal or alloy to come into intimate contact, i.e., at the crack tip, for these forms of attack to occur. In either form the normal ductility or the stress level necessary to produce fracture is greatly reduced.

In LMIE the most common result is instantaneous fracture of the solid metal while an applied or residual tensile stress acts along with intimate contact with certain metals at temperatures above their melting points. There are several critical combinations of susceptible solid metals and liquid metals that may produce LMIE. A very small amount of the melted metal is often sufficient to produce cracking. Liquid mercury (Hg) is likely the most common metal that can produce LMIE and this naturally follows since it has such a low melting temperature, i.e., -40 degrees F (-40 degrees C). In addition, other liquid metals with much higher melting points can also produce LMIE. These include zinc (Zn), cadmium (Cd), lead (Pb) and tin (Sn). Embrittling metals may occur in pure form or as alloys.

Some critical combinations that that can produce LMIE include carbon steel or low alloy steels and Cd, Pb or Sn; austenitic stainless steels and Zn, Hg or Sn; copper alloys and Hg, Sn or Pb; aluminum alloys or titanium alloys and Hg. Two of the more common incidences of LMIE are austenitic stainless steels exposed to liquid zinc or brass exposed to mercury.

SMIE has the same general effects on the mechanical properties of susceptible alloys, as does LMIE. Also like LMIE, in SMIE there has to be a specific combination of susceptible alloy and embrittling metal or alloy and a tensile stress (applied or residual) in the susceptible alloy. The major difference between the two forms is that in SMIE the offending metal is at a temperature below its melting point. However, it has been observed that the severity of SMIE increases with higher temperatures and is greatest at the melting point of the embrittling metal. Other differences between the two forms of embrittlement are that SMIE typically involves multiple cracks that grow slowly whereas LMIE involves a single crack that generally grows very quickly.

Some critical combinations that may produce SMIE are low alloy, high strength steels and Cd, Pb, Sn or Zn; copper alloys and Hg plus titanium alloys and Cd, silver or gold.

Corrective or preventative actions for either LMIE or SMIE can include the following:

Clearly, the first and best alternative is to avoid the specific combinations of susceptible alloy and offending embrittling metal whenever this is possible.

Electroplate or clad the susceptible metal after assuring that the barrier material itself is not an embrittling metal for the substrate.

Use a ceramic or a covalently bonded coating (generally polymeric) on the susceptible metal. Only materials with metallic bonding are susceptible to these two forms of attack.

Intergranular attack (IGA) - This form of failure involves preferential corrosion nearby the grain boundaries in susceptible alloys. Usually there is no or minimal attack of the interior of the grains themselves. The weight loss due to on-going IGA typically accelerates with time. This is because severe attack eventually surrounds individual grains and allows them to completely drop

out of the metal matrix. Figure 3 illustrates three relative levels of crystalline structure in metals, the relationship of individual grains to grain boundaries and the appearance of IGA.

As a prelude to IGA in an alloy, a metallurgical process occurs in which the composition at or beside the metal's grain boundaries changes versus the composition inside its grains. This occurs over a critical temperature range. After the alloy has experienced this change it is sensitized. The resulting heterogeneous condition is one of the classic situations that promote corrosion. Sensitized alloys must be exposed to specific corrosive media for IGA to occur. However, there are several alloys that can become sensitized and then suffer IGA in a variety of corrosive media.

Sensitized stainless steels, nickel-based and aluminum-based alloys can all experience IGA. The sensitized condition also makes many of these alloys much more susceptible to other forms of attack, i.e., general corrosion, pitting or crevice corrosion and intergranular SCC.

The classic example of sensitization and subsequent IGA occurs in certain austenitic stainless steels, e.g., Types 304, 316, 309, 317 and 302. The carbon content of these alloys is key to their susceptibility. Extended exposure to a temperature range between 1600 and 800 degrees F (871 to 426 degrees C) causes carbon in the alloys to preferentially join with the chromium (Cr) in the alloy nearby the grain boundaries and precipitate out of the metal's matrix to the grain boundaries. This greatly depletes the areas immediately adjacent to the grain boundaries of Cr. Chromium is the primary element in stainless steels responsible for the passive film that provides their resistance to corrosion in many media. The metal is transformed from a generally homogeneous condition to a heterogeneous one because of the adjacent differences created in composition. When the resulting sensitized alloys are then exposed to specific corrosive media IGA or another form of corrosion is very likely.

IGA in sensitized austenitic stainless steels can occur in a variety of acids, e.g., nitric, sulfuric, phosphoric, hydrofluoric, acetic, formic and also in seawater. The presence of certain oxidizing ions such as ferric or cupric ions in these acids makes for especially aggressive media for producing IGA. The sensitizing temperature range can occur during slow cool-down after welding, during various incorrect heat treatments or, sometimes, in service.

Certain nickel-based alloys are susceptible to sensitization and others are not. The manufacturers have produced many alternative nickel alloys that have evolved through multiple compositions to

**Body Centered Cubic (BCC) – Unit Cell
(Characteristic of room temperature carbon steel)**
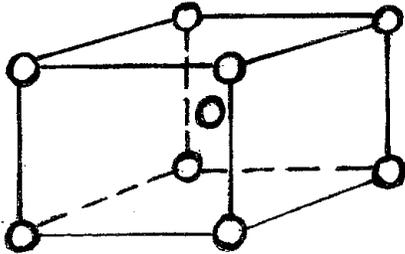
**One Crystalline Grain – Shown in Two Dimensions
(Typically includes hundreds of unit cells
in three dimensions)**
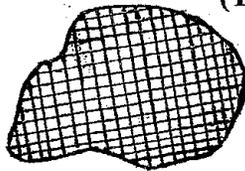
**Multiple Grains - Separated by Grain Boundaries
{Grain boundaries only visible after etching
polished metallic specimen.}
Wider grain boundary path indicates intergranular
attack (IGA) and/or intergranular cracking}**
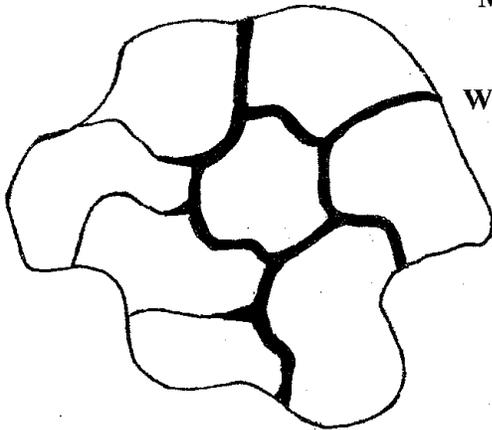
**Figure 3 – Schematic Representation of Three Levels of Crystalline,
Metallic Microstructure**

address the IGA problem while maintaining desirable qualities relative to other criteria. Alloy producers can provide current recommendations for the best alloys for a given application.

An alloy's carbon content is critical in resisting IGA in stainless steels as well as nickel alloys. The lower the carbon percentage present the less likely that carbon can join with a sufficient quality of chromium during exposure to the sensitizing temperature range to significantly deplete chromium nearby the grain boundaries. Thus one solution for the stainless alloys is to use grades with a controlled, maximum level of carbon such as Types 304L or 316L instead of standard 304 or 316. However, in most cases this presently is a moot point because most modern steel mill processes can produce dual certified grades, i.e., sold as 304/304L or 316/316L. These alloys have the desired low level of carbon, i.e., a maximum of 0.03 %, but still maintain the strength of the older 304 and 316 grades that have a maximum carbon content of 0.08%. A higher carbon content generally provides strength for an alloy so in the case of the dual certified stainless grades the carbon "deficiency" is compensated for by adding nitrogen that also adds strength but does not combine with chromium to produce a sensitization problem.

Another approach to IGA control is to use "stabilized" grades of stainless steels. These include the addition of titanium (Ti) in Type 321 or niobium (Nb) plus tantalum (Ta) in Type 347 in amounts dependent on the amount of carbon present. The Ti, Nb and Ta function by preferentially combining with the carbon present during sensitizing temperature exposures and precipitating to grain boundaries while leaving the protective chromium evenly distributed. For IGA control in nickel alloys, production processes that result in low levels of carbon are often combined with the addition of Ti, Nb and Ta. The stabilized grades of stainless steels are considered more resistant to sensitization than the low carbon grades when the application requires long-term service exposure to a temperature in the sensitizing range. However, when welded, the stabilized grades of stainless steels can be subject to a form of IGA known as knife-line attack. This can be addressed with the choice of welding variables used.

IGA can occur in aluminum alloys. Those alloys in the 2XXX, 5XXX and 7XXX series are most susceptible. This occurs due to precipitation mechanisms somewhat similar to the stainless steels but here the process involves movement of a portion of the copper or zinc or magnesium nearby the grain boundaries to the boundaries. Heterogeneous, electrochemical conditions are then established versus alloys that have retained their Cu, Zn or Mg in even distributions throughout the matrix of their grains. The 6XXX series of aluminum alloys are generally resistant to IGA.

Corrective or preventative actions for IGA can include the following:

Because many of the problems encountered with IGA involve austenitic stainless steels, corrective actions are most developed for these frequently used alloys. The best approach is to avoid the sensitizing temperature range (800 – 1600 degrees F) completely and, secondarily, if that is impossible, expose the alloy to that range for as short a period as possible. The latter may be pursued, for example, by using appropriate welding procedures that limit the time the metal spends in the sensitizing range.

Use low-carbon grades (or dual certified grades) or stabilized grades of austenitic stainless steels when exposure to the sensitizing temperature range and specific corrosive media that cause IGA are unavoidable.

Seek recommendations from manufacturers of nickel-based alloys for specific nickel alloys to resist IGA along with resistance to other forms of corrosion.

If an aluminum alloy is needed in a given application, seek to use one from the 6XXX series. If this is not possible, get advice from an aluminum alloy manufacturer.

Erosion-corrosion (EC) - This form of attack involves the co-joint action of a corrosion process and a flow-induced abrasive wear process together leading to accelerated loss on a metal surface. It produces more damage than either the corrosion or the wear process acting alone.

EC occurs in a wide variety of applications, e.g., in pipe and various pipe fittings, in flow measuring orifices, in pressure let down valves, on impellers of centrifugal pumps, in the tubes of shell and tube heat exchangers, on marine propellers, on turbine blades and on chemical manufacturing tank agitators. The macro-scale appearance of EC on an attacked surface includes grooves, waves, rounded holes and/or horseshoe-shaped features.

It occurs primarily in areas of higher velocities or impingement and particularly where there is turbulent rather than laminar flow. Often the damage is very localized to areas where these flow conditions exist. The damaging fluid may be a liquid or a gas. Solid particles in the fluid greatly accelerate the rate of attack. Slurries – particularly those that contain large, sharp particles – are well known as sources of erosion-corrosion.

Cavitation is a related process in which there is alternate formation and collapse of gas bubbles at or near a metal surface in a corrosive liquid. It is caused by high flow velocities coupled with large pressure changes. The collapsing bubbles create high impact forces on the metal surface so that plastic deformation and/or breaking off of metal particles occur. Rough, jagged pit-like damage is created. It can occur on pump impellers, on the propellers of marine vessels and in valves in which there is a large pressure reduction.

Passive films provide the inherent resistance to corrosion on many metals. In EC these films are locally damaged either by the abrasive action of the fluid flow or by the impact of collapsing bubbles in cavitation. While both abrasive wear and corrosion act in the EC process, materials that have a good corrosion resistance to the given fluid usually provide more resistance than those that provide only abrasive resistance. The ability of an alloy to reform its passive film after the film is damaged generally depends on the specific alloying elements and their percentages in its composition. Thus the overall corrosion resistance of an alloy in a given corrosive medium is the primary factor in its resistance to EC. Abrasion resistance is secondary.

Often alloys that are resistant to a given corrosive medium at zero or low flow conditions suffer EC when the fluid velocity exceeds some upper, critical value. An example is the response of carbon steel in high concentrations of sulfuric acid. Static, concentrated sulfuric acid is often safely stored in aboveground carbon steel tanks. However, a stainless steel or higher alloy must be used for pump casings and especially impellers to avoid EC when that same acid is pumped. Carbon steel has a much lower critical velocity to avoid EC as compared to the critical velocity for stainless steels and nickel alloys in several corrosive media. Because of this effect it is important when choosing a material to resist an unavoidable, EC condition to make sure that there are test data available that indicate corrosion rates as a function of velocity.

Corrective or preventative actions for EC can include the following:

Selecting an alloy that provides good corrosion resistance to the given electrolyte - at the maximum expected velocity - is likely the most effective control or corrective measure. This often means using an alloy that has a high initial cost but a lower lifecycle cost than alternatives.

EC frequently occurs in water systems where corrosion can be controlled with inhibitors. In these cases select and apply a suitable chemical additive. If feasible, lowering the service temperature is always helpful.

Do all possible to lessen the negative effects of unavoidable slurries. This means using strainers to filter out large solids and/or drastically limiting flow velocities.

Wherever possible, avoid very high velocities and areas where turbulence is created. This may involve diameter increases for piping plus avoiding short radius piping elbows and drastic reductions in pipe size over a short distance.

Pay special attention to the hydraulic design parameters employed for centrifugal pumps to avoid the possibility of cavitation. To reduce the possibility of cavitation at large pressure let-down points in a flow stream, use multiple, smaller pressure letdowns rather taking the pressure drop in one, large step.

Sometimes adding a barrier coating to a surface otherwise exposed to EC may be feasible. However, be careful that the coating has both corrosion resistance to the electrolyte and mechanical resistance to the abrasive wear component of EC.

 Dealloying –This form of failure, also known as selective leaching, involves the preferential corrosion of one element in an alloy. The remaining material is left in a greatly weakened condition. Attacked areas are porous and overall the alloy experiences a large loss of strength, hardness and ductility. Frequently exterior dimensions of the damaged metal are not changed and remain intact until the metal is touched or handled. There is no clear agreement on the mechanism that causes dealloying.

The most common example of dealloying is in brass alloys in which the zinc is preferentially attacked. This corrosion generally takes one of two forms. In the uniform or layer type a relatively uniform dezincification area occurs at the brass surface exposed to the corrosive medium while the metal below is not attacked. This form occurs frequently in brasses with a high zinc content when exposed to acidic media. The second type of dezincification, the plug type, occurs at localized areas of attack that penetrate into the metal. Plug type dezincification most often occurs in environments with neutral or basic pH values and high temperatures.

Dezincification generally occurs in brasses with more than 15% zinc. Tin (Sn) is often added to high zinc-content brasses as a means of inhibiting dealloying. The addition of small quantities, i.e., approximately 0.2 %, of arsenic (As), antimony (Sb) or phosphorus (P) to inhibited brasses provide additional protection along with the tin.

The second most common form of dealloying occurs in gray cast iron materials. This is correctly identified as graphitic corrosion (and not graphitization). Here there is preferential corrosion of the iron in the cast iron leaving behind brittle graphite flakes with very little strength. The attack is often very slow and may take a period of thirty or more years to progress to detectable levels. A relatively benign, aqueous environment is sufficient to cause the problem. It often occurs in underground, gray cast iron utility piping especially when the soil has much clay and when sulfates are present.

The common correction for graphitic corrosion is to change the material from gray cast iron to ductile cast iron or to malleable cast iron. Neither is generally susceptible to this form of attack. Ductile cast iron pipe is now routinely used for new, buried utility pipelines. However, there is still much buried gray cast iron that has been in such service for many years. If the soil around old gray cast iron piping has not been disturbed for many years it is not uncommon for the soil to harden enough to resist the relatively low internal pressures in many lines. Damage to the gray cast iron may not be detected until it crumbles or the original pipe breaks apart when an excavation disturbs the supporting soil.

Dealloying also occurs - but much less frequently than the first two forms - in other types of alloys. For example there is preferential attack in acids of the aluminum (Al) in aluminum bronzes (when the Al content exceeds 8%) or of the silicon (Si) in silicon bronzes. It's rare but there can also be preferential attack of the nickel in 70% nickel- 30% copper alloys used for heat transfer tubing at temperatures above 212 degrees F at low flow rates.

Corrective or preventative actions for dealloying include the following:

To prevent dezincification, use brasses with less than 15 % zinc. If this is not desirable use brasses inhibited against dealloying by the addition of tin or small amounts of As or Sb or P.

To prevent graphitic corrosion of gray cast irons use ductile or malleable cast iron as substitutes.

Microbiological influenced corrosion (MIC) – This category of failure includes the several ways that certain living microorganisms influence corrosion on metallic materials. The process and products of the life cycles of certain microorganisms create conditions that greatly accelerate corrosion when compared to the same service without the organisms. For example, different types of microbes produce acids that are detrimental to passive films or hydrogen that can

promote hydrogen-assisted cracking or hydrogen sulfide that can produce severe corrosion. Many types of microbes simply collect on a metallic surface as slime – called a biofilm – that by its presence alone creates conditions that lead to corrosion. Generally, all widely used metallic engineering materials are susceptible to MIC. Titanium alloys may provide somewhat better resistance.

MIC is common in many industries and applications. These include the interior of cooling water facilities, in fire sprinkler systems, on the exterior of buried pipelines, in chemical and pulp and paper manufacturing industries' equipment, on marine piers and in nuclear power facilities. Attack is greatly intensified in equipment where there is no flow or low flow conditions, e.g., inside pressure vessels after hydrostatic pressure tests when there is insufficient drainage of the untreated water used. Wherever moisture is present the potential exists. MIC is also often seen on the heat-affected zone (HAZ) of welds and on heat-tinted regions of welds.

MIC seems to occur by several processes but clear understanding of all the responsible mechanisms is elusive. Many explanations have been proposed and the scientific and engineering literature on the subject is large. It can be difficult to definitively identify MIC as the cause of a given corrosion failure rather than another form of attack. Often there is controversy among researchers that concentrate their efforts on understanding MIC.

Water and some form of nutrient to support the microbes are necessary for this form(s) of attack to occur. Nutrients can be supplied by carbon, nitrogen, phosphorus or iron. A biofilm attached to a metallic surface is often the starting point in processes that eventually lead to accelerated corrosion. Typically a biofilm consists primarily of water plus a complex mix of several types of interdependent microscopic organisms, nutrients for them, excretions from the microbes and loose debris. Once a thin, initial biofilm is attached to a surface, it provides an attractive home for additional microbes that move in the surrounding liquid. The movable microbes settle onto the biofilm, grow in number and thus make the film thicker and more robust. The biofilm or biofouling can be caused by bacteria but also by algae or fungi. Corrosion does not always occur under these deposits but it is probable.

Apart from corrosion, the common results or biofilms or biofouling in industrial applications are increased pressure loses in piping and/or drastically reduced heat transfer rates. Regarding the latter, this effect is easy to understand because the thermal conductivity of water, i.e., the major

component of biofilms, is approximately 1% of the value of steel. Adding a very thin biofilm to a steel heat transfer surface will obviously greatly lower the resulting rate of heat conduction.

The presence of a biofilm alone is often the cause of severe corrosion because of the obstruction it presents. On stainless steels this attack is crevice corrosion that appears as pits and on carbon steel the attack more likely will appear as general corrosion. Besides the crevice effect many bacteria create other conditions under the film that further encourage corrosion. On stainless steels the rate of pit penetration under biofilms can be amazingly high. Metal penetration rates in the range of hundreds of mils (1 mil = 0.001 inch) per year have been reported.

Anaerobic sulfate reducing bacteria (SRB) were the earliest class of microbes to be associated with MIC. SRB are often encountered in underground environments and in natural water systems. There are several other types of bacteria that can occur with MIC processes, e.g., acid producing, sulfate oxidizing and iron or manganese reducing bacteria. There are many additional types of bacteria that may be involved with MIC but what roles they play are uncertain.

Most bacteria cannot survive at temperatures above approximately 175 degrees F (79 degrees C). That temperature limitation is one indicator to use in a RCFA to determine whether MIC or another corrosion mechanism has occurred. Of course, there are many applications in which this temperature is not exceeded and so MIC can often be a possibility in failures.

Certain potential indications of MIC discovered during a failure analysis can be misleading. For example, ferric sulfide that is created during a sulfate reduction reaction on carbon steel produces a black corrosion product. Ferric sulfide is formed when SRB are active on steel but this compound can also be generated by other corrosion reactions when no SRB are present. Another possible indicator of MIC is the formation of voluminous, conical-shaped deposits – called tubercles - on the attacked metal surface. Tubercles often occur when MIC is present but they can also be formed when MIC is not active. On stainless steels the morphology of MIC often includes large pits with smaller pits inside each large pit. Frequently there is lateral penetration or "tunneling" from the larger pit walls (parallel to the exposed metal surface) into the metal. However, there have been incidences in which these morphological features appeared and it was shown that MIC was not involved. Thus depending on one of these possible indicators alone to identify MIC is not recommended.

The most definitive indicator of failure by this process is the confirmed existence at the attacked site of bacteria that are known to produce MIC. There are commercially available field kits that can detect the presence of specific bacteria that are generally accepted as being involved in producing MIC. However, the kits have to be used carefully to obtain reliable results. One problem is that a MIC process in a given failure may have been caused by microorganisms that the particular field kit was not designed to detect.

Often samples of corrosion product are taken in the field and sent back to a laboratory. There it is attempted to grow, i.e., to culture, and count whatever bacteria are present so as to show whether or not the bacteria that grow are ones known to be associated with MIC. This may also present potential difficulties, e.g., were the collection and handling techniques for the samples adequate and were the culturing medium and other lab conditions appropriate for all the bacteria present to grow and thus be counted?

There is a more recent laboratory detection technique that can be a good alternative to culturing. This technique depends on comparisons between DNA data taken from bacteria known to be associated with MIC (that have been stored in a database) and the DNA of organisms collected from an attacked metal surface in the field. Both the culturing and the DNA methods have advantages and disadvantages and, as in other areas of work on MIC, there is controversy about the value of each method.

Corrective or preventative actions for MIC can include the following:

Perhaps the most effective control measure in water systems is to keep all metal surfaces exposed to untreated water clean and free of deposits. Completing regular mechanical and chemical cleaning to keep surfaces clean is best. Direct examination to confirm this (or to take corrective action) during equipment shutdowns is the most effective method. Pay special attention to unavoidable dead legs in a piping system or other areas where flow rates are very low. Obviously, there are many applications where these actions will not be practical.

Assure that provisions are maintained for complete drainage of liquids in piping and equipment during shutdowns and especially after hydrostatic pressure tests where untreated water was used.

In underground applications, use a suitable coating that will act as a barrier to protect the metal substrate. Note that the plasticizers that are used in certain PVC coatings and the adhesives that

are used with some polyethylene tapes for pipe can serve as nutrients for bacteria. Assure that these possibilities have been eliminated during the coating selection process.

A variety of biocides, i.e., chemical agents that kill microorganisms, can be employed to control MIC in water systems. The vital factor in using these products is in correct and consistent monitoring of their efficiency in the given system. This must include regular inspection of corrosion coupons plus monitoring of the bulk liquid for a variety of chemical and biological parameters. Consistency of monitoring of the long-term trends or changes of these parameters provides the best indicator of the usefulness of a given biocide. Use of an experienced and knowledgeable biocide supplier is essential.

In approaching a failure analysis in which MIC is suspected, use the best available in-house authorities or outside consultants with specific knowledge and experience with this mechanism as well as other forms of corrosion. Understand that the confirmed presence of bacteria that are known to be associated with MIC is the vital indicator. Other indicators may not be reliable if taken separately.

If all other control measures fail, determine if the use of a titanium alloy is feasible in the specific application.

Wear –

This area of failure results in the undesired removal of material from a metal surface due to relative movement between the surface and a second contacting surface or objects. In most cases wear debris are generated and one or both of the moving, contacting media may otherwise be degraded. The active mechanism typically is plastic deformation and/or fracture at the metal surface but in certain forms there may also be a contribution from corrosion.

Wear is a complex failure mode because it can take various forms and because several factors often act simultaneously to affect the degree of damage that occurs. Some of the most important forms are abrasion, erosion, adhesion and fretting. Less common forms are cavitation and liquid-drop impingement.

Depending on the particular form of wear, the influencing factors include the bulk and surface properties of both the wearing and the wear-causing materials; several variables related to the

lubricant (if employed); corrosive conditions that may apply and operating variables such as temperature, forces at the contact interface, contact area and the speed of relative motion. Wear resistance is not a material property but, instead, is a result of the synergistic interaction of several parameters acting together in the given application. Because of this complexity, much more than the worn parts have to be examined to complete an effective failure analysis. A systems approach has to be used so that the interaction of the several possible causative factors is investigated.

Wear is common in the mining, earth moving and agricultural industries plus in metal machining and processing operations. It is also common in the great variety of dynamic machinery applications that involve rotating, reciprocating or sliding contact between machine parts. Partial or complete destruction of one or both of the contacting metallic surfaces can occur. A major concern is that some wear processes create surface cracks in the metal that can then lead to accelerated failure by fatigue. Other possible deleterious effects are changes to critical dimensions or profiles on metals; increases in vibration levels in dynamic equipment and clogging of critical flow passages by wear debris.

Abrasive wear involves the plastic cutting or plowing of a softer material when non-metallic (or sometimes metallic) harder particles contact the wearing surface and move relative to it. Generally, there is no lubricant at the interface. It is characterized by high shear or compressive stresses, low speed wear particles and grooves in the softer material. Wear debris are generally destroyed during the abrasion. It is commonly found in applications where hard, sharp particles act to abrade the metallic surfaces in contact with them, e.g., in ore handling equipment in the mining industry or on screw conveyors that handle materials that include hard, solid particles. Beneficial abrasion occurs in mechanical grinding and similar manufacturing operations.

Erosion is similar to abrasive wear. However, in this process the shearing force that degrades the metallic surface is provided by the kinetic energy of solid particles that are carried onto the wearing surface by a moving fluid – either liquid or gas. Low stresses (relative to abrasion) are created but the particles move at higher speeds. Larger and harder solid particles create the most damage. If the wearing material is ductile it is cut by the particles and typically grooves are formed. If the metal is brittle there is micro-scale fracture at the surface and small chips are formed. Erosion often occurs on fan blades, pump impellers, propellers on marine vessels and in pressure let down valves.

If the fluid is corrosive to the exposed metal - especially if the operating temperature is above ambient - erosion combines with corrosion. This is *erosion-corrosion* (EC) as discussed earlier in the **Corrosion** section.

Cavitation is a special form of EC in which there is alternate formation and collapse of gas bubbles at or near a metal surface in a corrosive liquid due to high-velocity flow and pressure changes. This also was discussed in the **Corrosion** section.

Liquid-droplet impingement is a form of wear that occurs because of the impact of liquid droplets on a metallic surface as they are conveyed in a gas or vapor flow stream. The droplets are commonly formed by condensation from a vapor such as steam as the temperature or pressure of the vapor decreases. Repeated impacts on the micro-scale projections from the metal surface, i.e., the asperities, are partially damaged and eventually break off. More metal is removed from the surface as the process continues. The appearance of the damage is similar to that of cavitation. It often occurs on steam turbine blades in the low pressure, "wet" end of the turbine.

Adhesive wear occurs where there is sliding contact between two continuous metal surfaces with poor or no lubrication separating them. Initially this allows micro-scale welding between the highest protruding asperities from the surfaces. As the relative movement continues, micro welds at the highest, protruding asperities break and new ones are formed. Wear debris are transferred from the softer metal to the harder one in the sliding couple. Frictional heat increases with time and thus an increase in temperature occurs. Several names are used to describe the various levels of adhesive wear on ferrous alloys (from least-to-most severe): scuffing, scoring, galling, white layer and, finally, seizure. The white layer term describes a surface layer of hard, brittle (untempered) martensite that forms due to the build up of heat. In steels complete destruction of interacting surfaces occur at temperatures in the range of 1600 to 2000 degrees F (871 to 1093 degrees C).

Adhesive wear failure can occur in any of the many mechanical applications where there is continuous, significant movement between machine parts that are intended to operate with a lubricant. The most important application parameter in the incidence of adhesive wear is the absence of a suitable lubricant between the moving surfaces. A good lubricant has to provide certain vital functions. It separates the two surfaces with a thin film, it dissipates frictional heat and it flushes out wear debris. Circulating lube oil must be continually filtered to remove solid

particles, it must be kept free of degrading contaminates such as water and it must be cooled to prevent excessive temperature increases.

The vital factors to consider in analyzing an adhesive wear failure are to determine if a suitable lubricant was selected and used correctly. The latter includes determining if adequate filtering and cooling of circulated lubricant was being accomplished. Specialists can derive much valuable information about such failures by analyzing the physical and chemical properties of the lube being employed and the solid wear debris that it may contain. The viscosity of the oil (at the intended operating temperature) as well the additives and any contaminates present need to be defined. Various laboratory techniques are used including energy dispersive spectroscopy (EDS), inductively coupled plasma (ICP), X-ray diffraction (XRD) and Fourier transform infrared spectroscopy (FTIR). Obviously, persons competent in the use and interpretation of results from these analytical techniques are needed to derive useful information.

Fretting wear is a form of adhesive wear in which closely contacting surfaces that are not expected or intended to move undergo extremely small amounts of relative motion. Typically no lubricant is present but that is not always true. Micro welding of asperities occurs and eventually powder-like wear debris are created at the interface. In ferrous materials the powder is iron oxide. This is reddish-brown in color and may be red if oil is present. In fretting of aluminum contacts the wear debris are aluminum oxides and their color is black. Because fretting wear debris are oxides, fretting is often known as fretting corrosion. However, the corrosion oxidation process is only incidental to the primary adhesive wear mechanism.

Fretting often is induced by vibrations that occur during operation of equipment or during transit and shipping periods when close-fitting parts are permitted to move slightly and rub against one another. It may occur in several applications, e.g., between bolts or pins and their holes; during shipment of rolling-element bearings at the inner bearing races; at press fits as in keyways on shafts or at coupling hubs; between tubes and their baffles in shell & tube heat exchangers due to flow-induced service vibrations in service and between the strands in wire rope that is subject to cyclic stresses.

A major concern with fretting is that minor surface cracks may be created on one or both of the contacting surfaces. If cyclic stresses are later applied to those surfaces premature fatigue failure often occurs as compared to the fatigue life of those same materials without the initial cracks being present. This is true, as previously stated in the **Fatigue** section, because the major

portion of the high-cycle fatigue life of a metal is consumed in <u>initiating</u> cracks. Therefore cracks created by fretting – often before the equipment is put into service - can significantly reduce time-to-failure in cyclic service stress applications.

Corrective or preventative actions for the different forms of wear can include the following:

General considerations

Proper material selection is the most common approach to resist several forms of wear and, in general, the critical material property is surface hardness. Material fracture toughness also needs to be considered. For adhesive wear, lubrication methods plus operating and design variables are essential to consider.

Typically high hardness materials offer the best wear resistance and soft materials such as copper and aluminum alloys are significantly inferior. In ferrous alloys such as steels the hardness attained generally depends on the carbon content and other alloying elements present in the alloy's composition and on the heat treatment processes applied. As the carbon content increases in ferrous alloys so too does the potential for the formation of hard, brittle martensite after rapidly cooling, i.e., quenching, the alloy from a high temperature in the austenitic range to a much lower temperature. Typically the material is then tempered (or exposed to a somewhat raised temperature for some period) to partially soften the material and regain some extent of toughness. Together these various heat treatment processes produce quenched and tempered steel.

Wear resistance is inversely proportional to the toughness of steel. Thus there is a trade-off between the final hardness and toughness in a steel to achieve optimal wear resistance. However, increasing hardness is generally desirable unless extremely high hardness values are obtained and thus the negative effects of low toughness act to lessen wear resistance.

Abrasive wear resistance can be obtained by several material selection options. These include the use of higher carbon and hardness steels; steels with tungsten carbide (WC) particles added to form a composite material; precipitation hardened stainless steels or particular austenitic stainless steels, e.g., alloy Nitronic 60 or high manganese austenitic steels; white cast iron with 20 % or more chromium and cobalt-based (Stellite) alloys. Other options are to provide case hardening in which a surface layer (of specified thickness) on the steel is made harder than the

lower metal by a carbonizing or a nitriding process; hard facing the surface with a weld overlay; or applying hard chromium plating to the wear surface.

Erosion, EC, cavitation and liquid-droplet impingement are all abrasion-related processes and so beneficial material selections for each are similar to those for abrasion resistance. For erosion resistance to slurries, soft natural rubber linings in piping and equipment provide good resistance if their limitations such as poor resistance to oils, sunlight, oxidizing acids and temperatures above about 150 degrees F are permitted in the application. Note that unlike metals a soft natural rubber is preferred for slurry resistance. In addition, resistance to these mechanisms is typically assisted by certain operating or design changes. Control measures for EC and cavitation were provided in the **Corrosion** section. Liquid-droplet resistance is generally obtained by material selection to resist this form of abrasive wear.

Adhesive wear resistance should always be evaluated in conjunction with the lubrication being used and the operating variables that apply. Proper lube selection as well as the measures taken to filter out wear debris, keep it free of water and other contaminants and control its temperature are critical. Often specialized assistance from persons knowledgeable in the many aspects of successful lubrication is needed. Although lubrication is the most important factor, the same materials mentioned above for resisting abrasive wear also apply to resistance to adhesive wear.

Fretting is difficult to control. Increasing the interference of press-fit components to lessen relative motion can minimize it but this must be carefully done to avoid other problems, e.g., overstressing the material or preventing a needed allowance for thermal movement. Other control measures might include using non-metallic materials between contacting surfaces to absorb vibrations, increasing the hardness of one or both contacting surfaces to prevent micro welding or fracturing of asperities, hard chrome plating one of the contacting surfaces or shot peening one or both of the contacting surfaces to minimize the initiation of fatigue cracks. Sometimes reducing the amplitude of vibrations that cause the small relative motion that produces fretting is practical. Examples of this include decreasing the spacing between tubing baffle plates in shell and tube heat exchangers or using impingement plates directly in the path of incoming flow from nozzles on the shell side of these units to distribute the force of the flow and thus reduce flow-induced vibrations.

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