Corrosion, Environmental Degradation and Surface Engineering

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Lecture – 18
Environmentally assisted surface deterioration- Part 3

Hello and welcome to the 15th lecture of the course on corrosion, environmental degradation, and surface engineering. This is the third lecture on environmentally assisted surface deterioration or degradation. In the first two slides of this lecture, I will attempt to summarize what we learned in the previous two lectures. Lecture 16 will focus on testing. Given that we have access to a variety of standards, what are the different testing methods available? We need to ensure consistency when presenting the results. So we'll start with that section from Lecture 16.

So probably this is the last lecture on environmental-assisted surface degradation. On the first two slides, I will be trying to highlight the important lessons we have learned from the earlier two lectures. Clearly, corrosion enhances the degradation phenomenon. What causes the material to become brittle and fracture more easily?
So even there is a wear debris which was supposed to have a lot of plastic built up and maybe the non-dimensional wear coefficient around $10^{-7}\ or\ 10^{-10}\ or\ 10^{-15}$. What does corrosion actually do? It raises the value to a point where the wear coefficient increases, making it impossible to determine the life cycle that would otherwise be possible. This is why we have explicitly stated that corrosion leads to the formation of brittle materials that fracture more easily. This corrosion can lead to the complete disintegration of the product, or it may cause the wear debris to chip off from the surface. As I mentioned earlier, high-cycle fatigue is the process that creates wear debris.

Under normal circumstances, the absence of corrosion and the presence of excellent environmental conditions may lead to the separation of all wear debris after approximately 1 million or 10 million cycles. Therefore, this phenomenon more closely resembles a high-cycle fatigue scenario. As corrosion takes hold, it will transform this process into low-cycle fatigue. Perhaps after 100 cycles of wear, debris will begin to emerge, and after 1000 cycles of wear, debris will continue to emerge. This process resembles a low-cycle fatigue mechanism.

It now functions more like a multiplication factor. Now, when corrosion occurs, it enables effortless removal from a surface. When the newly exposed surface comes back into contact with the environment, its chemical activity increases, leading to further corrosion. Therefore, these two processes, wear and fracture, are associated with corrosion, and their combined action may lead to a potentially fatal failure or damage to the surface. Now, when a new surface is exposed to a corrosive environment, it automatically undergoes wear or wear-related fracture, leading to the removal of debris from the surface.

Naturally, when debris is removed from a surface, a new surface gets exposed to the environment and subsequently corrodes. This phenomenon significantly increases the wear rate. By exposing new surfaces to the corrosive environment, the wear process can remove the corrosive product, speeding up corrosion and creating corrosion byproducts.

Another aspect to consider is the destination of the debris. When the surface degrades, particles emerge on the surface and can be treated as corrosion byproducts. These particles, resulting from corrosion and associated wear, can act as abrasive particles. This is why the wear coefficient, which might be around 10^{-9} under normal conditions, can increase to 10^{-6} when corrosion and wear interact. When corrosion, wear, and fracture are combined, the wear coefficient can further increase to 0.001 instead of 10^{-9}.

These phenomena are interconnected, which is why understanding them is crucial. In our earlier lecture, we described these processes in detail.

Another important parameter is friction. Whenever there is friction between two surfaces or at an interface, a pulling force or tangential load is required to move one surface relative to the other. Due to friction, energy is consumed and converted into heat. This frictional phenomenon or tangential load required for rotation or sliding also increases stress levels, which in turn increases shear stress and causes more surface damage. Higher friction forces result in a greater likelihood of surface damage. Conversely, with lesser or insignificant friction, subsurface cracks may take longer to reach the surface.

When friction is high, it's likely that cracks will surface instantly, leading to the removal of debris. This process will continue to generate more debris due to corrosion and related phenomena. Therefore, I can assert that tangential loading has the potential to intensify the degradation effects associated with wear, corrosion, and fracture. Therefore, if we take into account these three phenomena, along with friction force, and properly model them, we can design a product that is durable, highly survivable, and significantly reduces environmental degradation. In my previous lecture, I discussed how exposure to the environment degrades surfaces. Once the product sustains complete damage, it becomes a waste material, which in turn contributes to further environmental degradation. If we successfully integrate subsurface engineering into both the environment and the product, we can effectively prevent or reduce surface degradation, which also contributes to reducing environmental degradation.

We will be implementing both approaches by integrating surface engineering into the interface. So this has been mentioned, and we have already covered it. I am trying to just summarize. Now what is the major issue because in the previous lecture we covered a couple of case studies, and then we say the corrosion plays a very important role, particularly crevice corrosion and pitting corrosion, the reason being that we do not know where the crack is and how the chemical is really filtering into the surface and making some sort of hidden electrochemical cells. That is what recognizing and understanding finding hidden electrochemical cells in engineering a structure is like. So those bridges have a number of electrochemical cells; if we can really prevent those, then the life will be much better, or we may say that the life of the product will be like high cycle fatigue, or otherwise, because of the corrosion caused by the hidden electrochemical cell, the life will come down, or it may be reduced, and it will become low cycle fatigue. Therefore, it is crucial to recognize hidden electrochemical cells in engineering structures.

I am unable to comprehend the formation of the electrochemical cell at the surface, or possibly just beneath it. I am unable to recommend surface engineering tools or prevent the occurrence of corrosion. Therefore, preventing the collapse of the structure, as well as potential damage or rupture, is crucial. We also need to account for how much corrosion will occur and what the real relationship is with time. Initially, I am taking some factors as one, but over time, this factor is reduced. So can I really multiply that factor or corrosion-related factor with the strength of the material? And I say yeah, maybe at the beginning the strength is something like 100%; after, say, 5 years, the strength will be 90%; after 10 years, the strength will be 80%; and then there will be some sort of line available, or we say the threshold available. Now below this line, we should not use equipment; we should disintegrate, complete the bridge, complete the shape, complete the shape, or complete the plane, and then come up with a totally new system. We can analyze life only when we possess these factors and comprehend those systems.

That's why I suggest considering the decrease in strength of a structural component exposed to a corrosive environment as a preventive measure against structural collapse. This is a critical topic, so we have been focusing on it. We also conducted an exploration of a satellite operating in a low-earth orbit, commonly referred to as a LEO satellite. We discovered that this satellite could potentially cover two papers: one that utilizes a protective coating, specifically for temperature control, and another that employs an atomic oxygen-resistant coating. The operating temperature level controls the entire satellite, preventing damage to the surface and keeping the temperature within a specific range, thereby ensuring the proper functioning of our control systems. In the previous two lectures, we discussed the need for these coatings to lessen surface deterioration and degradation, particularly in low-Earth orbits. As I mentioned in the earlier lecture, in a low-earth orbit, we have many, many pollutants; atomic oxygen is one of the major thrusts.

Another thing satellites need to have is a high speed, and when we were discussing the Titanic case, we said that because of the ship's high speed (22 knots) and the fact that it is striking a very big iceberg, the damage will be very high. The velocity sensitivity is very high in this situation. Therefore, when operating a vehicle at such a high speed, it is crucial to exercise extreme caution, gain a comprehensive understanding, and propose a more effective coating. This is why, in both cases, researchers have recommended the use of nano coatings, as even a slight increase in the material's weight can lead to further complications. Therefore, we prefer not to utilize a minuscule or infinitesimal coating that ensures flawless distribution, no delamination, and no internal bubbles. Therefore, the use of such coatings requires sophisticated technologies to solve this problem effectively. So, this is what we have covered.

Now, on the second slide, we are reiterating the points covered earlier. Here, we emphasize that environmental variables are significant contributors to surface damage. As previously mentioned, there is an interplay between wear, corrosion, and fracture, where these three mechanisms collectively lead to major issues. Sequentially, wear degradation results in scratches, pitting, grooves, or other types of defects.

So wear is creating problems like this on the surface. Fabrication-related issues may also arise, but deformation, other processes, or relative sliding can cause surface scratches, pitting, or even grooves. Once those are there, the corrosion plays the most important role. We say corrosion takes advantage of these voids or whatever the deformation of pits on the grooves, and then allows to generate an electrochemical cell there. When this type of crack occurs, the electrochemical cell forms on those surfaces. This, in turn, may facilitate the propagation of an auxiliary crack. As this crack propagates, a natural fracture ensues. This fracture then divides the surface into two or more segments, a process known as fracturing.

In this form, wear, corrosion, and fracture operate sequentially. It may be slightly different, but I thought maybe this is the best way to present how these are linked with each other, how they amplify each other, and then what are the really important factors? We have learned that chemicals, water, humidity. we use the word acidic form or we say pH value less than 7, will be important; an increase in temperature or an increase in heat is really going to increase the wear rate. If there are crevices, or maybe the joints, as I mentioned in the case of the bridge, if there is a joint naturally, there is a problem because most of the time we follow the fabrication process, we do not really measure everything properly, and there will be some sort of crevice, some sort of gap in the earth sufficient for the corrosion to take place, the electrochemical form to form, or the cell to form there. The severity of this issue varies depending on the specific environments, but joints are also a major concern. Therefore, developing a product without joints would be ideal. However, as previously mentioned, the cost of fabrication would be significant, and we also need to ensure its cost-effectiveness.

Of course not for the aircraft; those are the systems where the cost does not really matter that much, but other things matter a lot if there is a casualty. So, the socio-economic effect plays a major role there. So in this case, another one I may also mention is that there are some sort of pollutant, contaminants, all of which will affect the atmosphere and environment. So, everything together has a real impact on surface degradation. Now, due to the inevitable surface degradation, we observe that chipping occurs at a significantly faster rate, resulting in a change in size.

Sometimes, we find that a shape is broken into several parts within a system, leading to significant changes in its structure. Even if everything appears to be in mild condition, the overall efficiency, which we require to be around 95%, falls short. This inefficiency renders the product useless to us. For instance, if we need a certain torque, say x Newton meters, and we don't achieve x torque, the motor cannot operate, and the unit becomes non-functional. As a result, we lose crucial functions and valuable features, making it pointless to continue using the product. We need to replace it, even if it hasn't completely failed or fractured into multiple parts. The loss of ability to perform valuable functions is enough to deem it ineffective. This is why we say that machine aging is influenced by the surrounding environment or atmosphere. Failure, as I mentioned, isn't limited to fractures; it also occurs when efficiency drops below a certain threshold, be it 95%, 90%, or even 85%.

If we define a specific value and are unable to achieve that level of efficiency, the product is considered to have failed. Failure doesn't necessarily imply parts breaking or numerous parts failing, but it could also indicate that the product isn't delivering the expected performance. Nanocoating can protect another surface from wear, corrosion, and fracture. Of course, microcoating is also available, but now, with the latest technology, we are talking about nanocoating, and the coating thickness should not exceed a certain limit. After removing the coating, we may need to consider refurbishing or reconditioning the products. Specifically, during our discussion of Leo satellites, we mentioned the significant benefits of nanocoating. Therefore, we can manage these corrosion and fracture phenomena through the application of nanocoating.

Nanocoating is a type of nanocrystalline deposit that can be crystalline or non-crystalline. What will happen is that it will increase the hardness of the surface as the wear rate reduces, and then that is why the wear rate comes down, and then the wear rate is coming down, and then there is a possibility to prevent the corrosive or chemical attack on that, and there is a possibility to reduce the fracture. Furthermore, if the nanocoating exhibits minimal friction, the majority of objects will remain below the surface, avoiding exposure to the corrosive environment. So, life will be extended. This is why we recommend mitigating corrosion by passivating surfaces and isolating contacting bodies. So, this layer or surface engineering layer comes between the product and environment, and that is why we use that this is the latest technology. Related nanocoatings are important to understand, and we will be covering in detail some coatings when we start the lecture on the coating or surface engineering.

So, we can say that coating and surface modifications are the most common, or maybe more useful, tools in surface engineering, and when we discuss the topic of surface engineering, we will return to these topics. Another thing is that when a major metal part is a site of brain-storming related, we say that when the phenomena are happening and we have a better understanding of those phenomena, then why not go ahead with this kind of thing? We say there is a big metal structure, and in the previous lecture, we said there will be some life, possibly 20 years, 25 years, or 30 years. So, for example, if I design a ship for 25 years, after 25 years we need to really dismantle the ship, or we have already learned how many times the big units are dismantled and then given to further processing. The process of remelting and reusing them necessitates significant effort.

Instead, what if I knew how to chemically degrade the product in a well within a time frame of, say, 10 hours, 15 hours, or 20 hours? Regardless of the detrimental impact of corrosion, why not apply this scientific knowledge to transform it into a productive or efficient process? Therefore, it is evident that maintaining a large metal structure, such as a ship nearing the end of its lifespan, can yield economic benefits. I'm using the word economically beneficial to describe the use of science to really That's why I suggest programming it for self-destruction; if the product has the ability to self-destruct, I would expose it to the environment. Our advice is to avoid atmospheric exposure, but there is a product we must demolish or break down. Why not implement a corrosion environment to facilitate the self-destruction of the units? This is a more manageable part, and we could potentially divide a complete system into multiple parts. In recent years, most countries, including India, have adopted the practice of dismantling old ships using manual labor or by hiring low-cost labor.

But why do we really need it when we have scientific solutions that will result in a much faster pace? Additionally, if we obtain a product in a highly functional form, we can perform a reconditioning function, which allows us to remove any non-functional components and potentially remelt and reuse them. So, this is why I believe that when we understand the science, we can best use it for the product minor. Not only is it important to prevent corrosion and failure, but it's also crucial to apply scientific modeling whenever necessary to reap significant benefits. Now, let us begin today's lecture with a few other aspects or factors. We are aware that ozone, as we have heard numerous times, can have harmful effects.

The question arises: how does ozone play a role in degrading the surface? So, that is why this topic says surface degradation due to ozone, and what is real ozone? You say mostly that ozone comes in a natural environment in the earth environment. However, we also know that there are a number of other activities than human beings, like a number of industrial processes, a kind of pollution that also releases ozone. Ozone is considered a highly active element of oxygen. Basically, ozones are highly reactive gases that undergo a series of chemical reactions due to their high chemical activity, potentially causing damage to the entire molecular structure.

We are well aware that ozone significantly damages any carbon or organic material present. We're explaining that in the rest of this slide. We assert that the degradation process of ozone follows a cyclic mechanism. Therefore, the degradation process of ozone follows a cyclic mechanism; it does not occur immediately, nor is it limited to a single movement. Rather, it is a continuous process in which the ozone molecule reacts with a double bond, particularly in a material containing carbon, such as an organic polymer chain. In these situations, oxygen plays a crucial role due to its high chemical reactivity, transforming the double bond into a single bond. The result of this reaction is the creation of a functional group.

So, once a molecule takes on a specific form, it increases its chemical activity, disintegrates at a single bond, and becomes significantly more reactive. Additionally, it contains an oxygen-containing functional group. This means that even within the polymerized structure, the functional groups will initiate subsequent reactions, leading to the presence of ozone. So, oxygen is also there. So, that is why there is a chain reaction; a continuous reaction will be there, and then it will speed up the degradation process. Organic materials like rubber, plastic, and the number of paints also degrade because of the ozone. Because of the exposure to the ozone, these materials are very vulnerable to ozone-induced surface degradation. Now, I am just trying to explain only based on the ozone, and then one of the materials, like rubber, is so reactive that it makes a number of cracks, or we say a network of cracks. Therefore, rather than fracturing into two pieces, it rapidly develops numerous cracks, leading to disintegration, which is why we refer to this phenomenon as ozone cracking.

Of course, we refer to ozone cracking, crazing, surface degradation, loss of flexibility, and the absence of a readily available or potentially connected network. The strength of the rubber material becomes almost negligible after exposure to ozone, which is a classic symptom of ozone lead degradation. So, what are the symptoms? Cracking, crazing, surface decoration, loss of flexibility, and then a continuous decrease in strength. If these features are present, we need to investigate the cause of the damage. We need to identify the source of the ozone leak, after which we can conduct a chemical examination of the affected surfaces. According to previous lectures, whenever there is degradation damage, we proceed with some sort of analysis, or maybe SEM analysis or EDX analysis, and try to figure out what has happened to surface. This enables us to avert additional harm, potentially in the future, or implement necessary product upgrades or material changes.

Another point is that if the concentration of ozone increases or temperature increases, or if there is a longer exposure time, the degradation will be much larger. So, there are three factors: the concentration of ozone increases with more and more damage; the temperature increases with more and more damage; and the time to exposure increases with more and more damage. So, this is related to ozone, and then there is one case study available in the literature; maybe there are many more, but I just picked up on one case study that was published in 2022, and what they have done is use alkali lignan. The nomenclature for this alkali lignan has already The alkali lignan (AL) incorporates carbon and subsequently undergoes ozone exposure. bjected to ozone. How was it subjected to ozone? They use ozone generators, which are available in the market at a cost-effective price. Often, we need oxidation and water cleaning services, which are readily available and not difficult to find.

They exposed the system to ozone at a concentration of 85 mg/l with a flow rate of 3 liters per minute for 45 minutes. The temperature was maintained at around 45 degrees Celsius, although this detail might not be mentioned on the slide. Additionally, they compared the effects by varying the pH levels to 3, 7, and 12 to determine the impact under different conditions and to understand what is happening.

In this study, several conditions were analyzed: no ozone exposure (Al AL), exposure to ozone with Alkali lignin (AL PH 3 OL-pH 3), and different pH environments (pH 3, pH 7, and pH 12). The researchers aimed to observe the effects on the material under these conditions.

For AL, with no ozone exposure, the surface appeared very clean with only minor debris in a few places, around one micron (1µm) in size. In contrast, AL pH 3 OL-pH 3, which was exposed to ozonated lignan in an acidic environment (pH 3), showed significant surface damage. There was a notable increase in surface roughness, major deformations, and numerous cracks. These damages were attributed to the ozonation and the low pH environment.

Now, if the pH value increases, then in this case, particularly if pH is kept at 7, the deformation is much less. So, even in the neutral environment, PH7, what we were showing in the acidic environment now even the neutral environment, ozone, is really acting on that. So, it is not only the chemical, but basically the major damage is happening because of the ozone. You are able to find out that there are a number of debris and more cracks, some of which are brittle fractures. Well, even coming to the basic nature of alkali nature, we are also able to find out the faults, or maybe the surface damage. Of course, if I compare naturally, I will say that this is the original surface where the where the least damage will happen when there is an alkali nature, or maybe the environment is alkali, or maybe the basic nature.

While coming to neutral, there will be some damage, and then when coming to acidic, there will be severe damage. So, ozone, naturally, in the presence of a corrosive or acidic environment, will really be affecting the surface. So, we should avoid this kind of exposure, and that is when the ozone really damages, and in this case, we are comparing that ozone in the presence of an acidic environment damages much more compared to the neutral environment or the basic environment. Then we are trying to cover the second case study, which is available and we have picked out from even journals published in 2019, and fortunately, this topic was covered when we were covering the corrosion topic, and we say crevice corrosion is important. We say that people mean localized corrosion; instead of going for localized corrosion, we should divide it into pitting corrosion and crevice corrosion. This case study focuses on crevice corrosion and its effects on P04L stainless steel. Chlorine, particularly in marine environments or coastal areas, significantly contributes to this type of corrosion. Chloride ions are more prevalent in these areas compared to normal environments.

Surface degradation caused by chlorides is a major concern, especially in coastal or marine locations, industrial sites, or anywhere with high chloride pollution. Chloride ions have high chemical activity and can penetrate the oxide layer that normally protects the steel surface. In the presence of chloride, this protective oxide layer can become compromised, leading to the formation of crevices and increased susceptibility to corrosion.

So chloride ions are easily able to penetrate that protective oxide layer. So, from the top, while we figure there is a good oxide layer, because the crevice is very small, maybe say a miniature dimension, chloride will pass from that surface, and when it does, it will directly go to attack the metal surface. They will replace that in the form of metal chlorides, and then metal chloride has, as we say, basically corrosion. So, it is not a protection, and after that, the really complete system is changing from a protective environment to a corrosion environment. Naturally, the damage will be very high, and then we need to consider from that point of view whether this chloride will produce pitting corrosion or crevice corrosion. So, crevice corrosion is also important; pitting corrosion, or some, maybe depends on the material and situation, additional circumstances, or maybe location, where things will change.

The literature indicates that not only metals are affected, but concrete structures with steel reinforcement are also vulnerable. Chloride ions have a high infiltration rate, allowing them to penetrate the concrete cover and reach the embedded steel reinforcement. This phenomenon is known as chloride-induced reinforced corrosion. This process weakens the steel reinforcement, compromising the integrity of the structure. To prevent such failures, proper precautions are necessary.

In the case study referenced, the authors examined excess material and used canisters as barriers, particularly for nuclear fuel. They aimed to provide a protective coating to prevent the exposure of nuclear fuel to the environment.

So that is why they use the excess canister, and then however they found that this kind of canister or this kind of material is subjected to localized corrosion, that is what we call pitting corrosion or crevice corrosion, and then that particularly in a sea environment where there are more chances of chemical ions. So that has been reported, and this paper has tried to figure out what the effect of this kind of corrosion will be. Of course, the composition of 304 stainless steel has been given a very low percentage of carbon and a and a relatively high percentage of silicon, and then chromium has been kept very high, nickel has been kept very high, and manganese has also been kept very high. So, in this case, it is a really good material, or it should have good chemical resistance, but unfortunately, because of the phenomena or because of the chloride ion environment, it fails, and that is a major issue. So, they did an experiment to find out the real impact of the chloride attack on this material.

So they use it sort of in the smoothening of the specimen because there are some standards for how to conduct these experiments, which we will be covering in the next lecture. How to perform the test: what are the different methods available? So as per those standards, the surface should be uniformly polished, whatever the sample they were choosing, and this topic was also covered in our earlier lecture, which was delivered on corrosion. So, they use M6 bolts and then different kinds of polymers, which really allow the crevice corrosion to form and then allow the infiltration. And then they also maintain the torque value, which, as per the standard, they kept out as 1.13 Newton meter to create a complete sample, and so that gets subjected to corrosion phenomena, and then using the electrolyte may be based on the sea water, and they synthesize sea water also that is as per the standard, which has also been mentioned as ASTM D 1141-98, and they use NCL 58.5% and other compositions as per these standards. So they follow the norms, and now in this slide, particularly, we are representing the results. So what are the results? This has already been covered in our previous lecture on how to form the specimen and how to get connected. Finally, this unit will be subjected to corrosion in an environment, and those units were also shown in our previous lecture. So this is what Albin and Meghan discussed, and they kept a temperature of around 45 degrees even in a marine environment. Now they tested three things when they kept the concentration very low, something like a 0.1 gram per meter cube, then they tested it for around 5000 hours, and then this is for 45% humidity, this is for 55% humidity, and this is for 70% humidity, and this is fine, as shown in the results when there is a 45% humidity. I am able to see more damage to the surface when the humidity increases to 55%. I find the least damage is 70%, but there is an increase in the damage to the surface.

When examining the microstructure in this case, we observe varying levels of damage: high, low, and moderate. The authors of the study aimed to demonstrate a specific relationship. They found a critical combination of humidity and chloride concentration, using 0.1 grams per cubic meter (0.1 g/m^3). The study showed the most damage at 45 degrees, the least damage at 55^0 , and significant damage at 70^0. However, when the chloride concentration increased to 1 gram per cubic meter (1 g/m^3), damage was observed starting from 45 degrees onwards.

So it depends on what kind of combination we are using, what the humidity level is, what the percentage is, and whether overall chemical reactions are important. So if you are able to model those chemical reactions and simulate them, we will be able to really figure out how much damage will happen to the surface. Again, we cannot remove complete damage, but we can minimize it by understanding science, understanding the mechanism, and understanding the simulation modeling of this kind of component or process. So that is why we can say here that due to the low chloride concentration of 0.1 g/m^2, a more humid environment is required. So that is why I say 70% humidity is very essential in this case; it may also be required to transport and filter the chloride into the crevices. So this is important, as I say that the humidity and percentage of the chlorides work together, and then maybe if I increase the temperature to 45^0, but if I increase the temperature to 70^0 , this will be slightly different. So that is why we cannot do so many experiments, so that is why we really require some sort of testing, and we will be covering that kind of testing from our next lecture onward. Now there is another study on something like sulfuric acid, and earlier in the lecture, I mentioned that even when the sulfuric acid concentration is very high, it may not harm the product that much. Of course, it can harm the human body, but it cannot harm the product as such. Many times, to make an electrochemical reaction, they really required water, or maybe they required appropriate electrolytes.

In this case study, the authors compare sulfuric acid with citric acid. Citric acid is a common acid widely used in the food industry. The study first investigates how sulfuric acid enters the environment. Atmospheric sulfuric acid forms when sulfur dioxide, a pollutant released from various sources, is emitted due to industrial activities and fuel combustion in automobiles. When sulphur dioxide mixes with water, oxygen, and other molecules in the environment, it forms H_2SO_4, which has a strong acidic nature. Previous studies have shown that the presence of acids can significantly impact the environment, particularly in the presence of ozone.

Acidic conditions significantly exacerbate this problem, particularly by making aluminum soluble in the soil. The researchers aimed to investigate how aluminum dissolves in H_2SO_4 and how this process impacts soil, potentially posing hazards to plants. Understanding these conditions allows for necessary preventative measures.

In this study, they used aluminum alloy 6061 and an electrolyte in sulfuric acid (H_2SO_4). They tested four solutions: sulfuric acid (SA) and citric acid (CA). Specifically, the sulfuric acid solution was applied with a current density of 1 ampere per square centimeter (1A/cm^2).

B has been used with a with a higher current density of 7.2. So this is a 1, this is a 7.2, and they showed that even at the same concentration, same operating temperature, and same time, if I am using the current density or increasing on the higher side, it is really affecting. 7.2 is actually causing more damage, and unfortunately, citric acid is showing a more dominant factor compared to sulfuric acid. So it is a case where we assume the sulfuric acid really will act much more severely, but in this case we are able to find more damage because of the citric acid, and that is why, of course, in both cases B and D. We find that the higher current density leads to increased porosity and superficial cracking, while citric acid, one of the most commonly used acids in our food industry, has a greater impact. Therefore, it is crucial to consider the impact of various environmental factors such as the outside environment, sulfuric acid, the inside environment, and potentially citric acid. We must also carefully consider the potential effects of the various chemicals we use, including polymers, on human health overall.

As previously mentioned, I want to highlight another important topic that was covered in the discussion on corrosion, which has a more significant impact than other chemical activities: hydrogen embrittlement. This issue is becoming increasingly critical and challenging to address. Although we have discussed hydrogen embrittlement before, let me summarize it again.

Hydrogen embrittlement is typically triggered by atomic hydrogen, significantly reducing material strength. Similar to how rubber deteriorates, developing numerous cracks and losing flexibility in the presence of ozone, hydrogen embrittlement causes materials to lose their essential properties, such as elasticity and damping. The material essentially becomes brittle and fails to perform its intended functions.

So the same thing is true in this case: most of the metals lose the most of their properties because of the hydrogen embrittlement, and then they cause an unexpected fracture. That is why this is very important to consider. Furthermore, this phenomenon is increasingly prevalent in the aerospace, oil and gas, and automotive industries. So whatever the main important industries, hydrogen embrittlement becomes common in those kinds of structures, and it causes a real damage to a structure element and then an associated risk for human life, because these are all the major units, and then human lives are one way or another related to those units. So really cause more damage to human life, and then of course products get disintegrated, and then maybe oil, fire, or some sort of debris comes in a million pieces, naturally affecting the environment. It is evident that hydrogen embrittlement leads to accelerated surface degradation, and despite low stress levels, failure still occurs.

This mechanism becomes very important for understanding material failure. Hydrogen atoms often originate from common sources, such as corrosion. For example, during the reaction between iron and water, or rusting, water dissociates into hydrogen ions (H^+) and hydroxide ions (OH^-). The free hydrogen atoms can then penetrate the material's surface. If this imbalance is not addressed through proper procedures, atomic hydrogen can infiltrate the surface. Hydrogen can enter the material during processes like corrosion, electroplating, or exposure to hydrogen-enriched environments where the product is stored for extended periods. So in this situation, what will happen is that this atomic hydrogen will infiltrate through the substance, and then, as a major problem, it will enter the lattice structure of a metal and keep closer to the grain boundaries. Grain boundaries are already fragile structures. We know that even the corrosion will affect the grain boundaries, but here the hydrogen is really getting clustered around the grain boundaries; naturally, the damage will be more, and moreover, this becomes more like a microstructural defect, and that is why there is a possibility of an abrupt fracture. And in my previous lecture, the corrosion takes a little longer, but somewhat hydrogen embrittlement is slightly faster than normal corrosion. That is why it really requires more attention in the present, and that is very important for a number of industries that are directly or indirectly related to hydrogen in one way or another.

So this is what we say: it really goes ahead with the hydrogen-induced cracks, and then even the expansion of cracks or propagation of cracks is also very fast. So that is why it is very important, and just this portion has been written to give again exposure because hydrogen is frequently created during corrosion reactions. That is why many people believe that hydrogen embrittlement itself is a part of corrosion. Again, in my opinion, hydrogen embrittlement occurs at a faster rate than corrosion. Therefore, defining hydrogen embrittlement as a distinct category allows us to concentrate more intently on preventing its occurrence. And then, in one of the common reactions we see, corrosion of iron in water results in the reduction of hydrogen ions, maybe OH ions, and then the form in this situation, and we can allow the hydrogen embrittlement.

Another important point is that hydrogen atoms diffuse through the material and condense at internal imperfections, such as cracks or grain boundaries. These weak planes are particularly susceptible to damage, and hydrogen embrittlement exacerbates the problem more than simple corrosion or other discontinuities. If not properly managed, this can lead to significant loss of strength, causing the material to fail at much lower stresses than it was designed to withstand. Therefore, it is crucial to model hydrogen embrittlement accurately and develop solutions to mitigate its effects. Numerous units have experienced issues due to this phenomenon, and we will cover related case studies in surface engineering.

In one case study, as discussed in a previous lecture, corrosion can transform high cycle fatigue into low cycle fatigue, shifting the failure mode from ductile to brittle. This slide illustrates the impact of hydrogen on fracture morphology and fatigue failure mode, transitioning from high cycle to low cycle life. Both figures show the fracture surface, with one exhibiting a cone and cup shape typical of ductile failure, while the other, subjected to hydrogen embrittlement, does not show this characteristic. This difference highlights the significant impact of hydrogen embrittlement on tensile testing results. Without hydrogen exposure, we see the typical cup and cone shape and microvoids indicative of ductile failure, as previously mentioned.

They developed MCV, displaying characteristics of a ductile failure. This is why Figures A and B illustrate the normal high cycle fatigue phenomena observed in this case. In the second case, where the specimen was subjected to hydrogen charging, the temperature was maintained at around 45^0 C. This resulted in a shear failure at a 45-degree angle. Additionally, numerous pits, fractures, and elongated cracks were observed, indicating a completely brittle failure.

Examining the SEM image reveals small dimples, but the predominant failure mode is brittle, with bridges and surface features visible. There are many quasi-cleavage macro voids rather than micro voids, as well as both primary and secondary cracks. Intergranular cracking also occurs, indicating significant strength reduction at very low stress levels. Both figures are shown at 1 mm and 10 µm scales, magnified 100 times, highlighting these issues due to hydrogen embrittlement. Testing has shown that these failures occur much faster.

At normal or lower temperatures, failures are evident, but the situation worsens with increasing temperature, whether from the external environment or internal mechanisms like friction. Higher friction forces require more energy, converting to heat and potentially raising the temperature. Thermal cycling, varying from 0 to 50 degrees, 50 to 100 degrees, or 100 to 150 degrees Celsius, due to environmental changes or loading and unloading, exacerbates the issue. This thermal cycling, combined with oxidation, corrosion, or hydrogen embrittlement, increases the damage.

A case study on turbine blades, referenced from a 2016 publication on thermal-mechanical fatigue investigation of a superalloy used in turbine blades, illustrates this. The study, titled "Temperature Assisted Oxidation," explains that the presence of oxygen and temperature significantly increases the formation of the oxide layer, causing more severe damage under fatigue loading.

In this instance, they've maintained two temperature conditions, one of which ranges from 500^0 to 1000^0 , indicating a fluctuation. They've kept the cyclic variation below 500^0 , and they discovered that, specifically, the life cycle decreases by half. When the temperature rises to a certain point, it leads to a reduction in the life cycle. In this case, naturally, the life cycle of this is something like 4675, maybe a number of cycles, and this is just half. So, what is really the difference? When we detect a ductile failure, we detect a secondary crack, which we then identify as a fatigue striation. However, when they reach this one, they find more under the ridges and a greater possibility of fracture, and that this is an expansion of this portion only has been assumed in this way. So, when the temperature increases, fatigue life comes down significantly, material properties also get deteriorated, and then we are able to find out with an increase in a material. The first question arises: should an increase in material make it more soft and ductile? However, this is not the case when thermal cycling occurs, resulting in a lower temperature. This, in turn, causes a type of fatigue, particularly at the fracture or brittle sites. So we say there is a strong dependence between temperature and oxidation, and an increase in the oxidation environment causes a reduction in fatigue life. Therefore, we can conclude that oxidation deteriorates at high temperatures, indicating the presence of numerous cracks at the site.

So the dissociation there are more possibilities there other than go for high temperature more and more cracks get formed, and then the pieces maybe the material which is very kind of super alloy material will get disintegrated and will have a much shorter life compared to its expected life. Temperature-assisted oxidation, temperature-assisted corrosion, or temperature-assisted hydrogen embrittlement. There are numerous environmental factors that interact with each other, or even become supportive of each other, and it is crucial that we approach this topic with a comprehensive understanding. o this is my last slide. Thank you for your attention.