

Corrosion, Environmental Degradation and Surface Engineering

Prof. Harish Hirani

Department of Mechanical Engineering

Indian Institute of Technology, Delhi

Lecture – 10

Heat and Radiation on surface degradation

Hello and welcome to the eighth lecture of the course on corrosion, environmental degradation, and surface engineering. The topic of this lecture is surface degradation mechanisms due to heat or radiation action. Now I can also say heat and radiation action, but we know very well that heat itself can damage the surface, radiation alone can damage the surface, and of course heat and radiation both can damage the surface. So that is why the title has been kept as a surface degradation mechanism due to heat or radiation action. There are three main phenomena in that it may have a completely different temperature and may be related to photochemical or somewhat high-energy radiation. The first question is: why do we study this topic at all? Is there any need? Yeah, there is a need.

The reason is that radiation and heat have a wide variety of effects on the materials, from simple heating to radiation-induced deterioration. Heat alters the physical and chemical properties of materials. Radiation can produce faults in a material's atomic and molecular structure, which can add up over time and lead to material failure. There are many ways in which materials can deteriorate when exposed to heat or radiation.

This lecture is meant to help students understand those processes. This is not a detailed lecture; it is only one lecture on which we are focusing. There will be a number of references, and there are books available. If you are interested, you can deal with or maybe refer to those books also. But our aim is to introduce the topic.

Now let us start with this lecture. What has been mentioned here is heat, which is very similar to the word heat or radiation, or I can say heat plus radiation. So there will be a total three kinds of failure mechanisms. Now, individually, I am using the word thermal heating. Individually, we use the, which in this case is UV or other radiation. UV is one of the most common available. Maybe we have a good understanding of UV.

So starting with thermal heating, we know it is going to change a microstructure, and we will cover a couple of examples and indicate even simple examples that we have already covered. We are trying to highlight or review those examples and indicate, yes, how thermal heating is changing the microstructure. Now, microstructure or change can be grain-related; it can be grain deterioration or grain growth; it can recrystallize the metal, maybe from one form to another; and there is also the possibility of phase transformation. It can also be melting, which we studied in one of the previous lectures. When exposed to the sun, UV, or another kind of radiation, it can cause localized heating. Now, this localized heating can cause damage to atomic and molecular structures.

It can cause melting also, or in the third one, we are saying that maybe some atoms are getting migrated from one surface to another. So what we say is radiation-induced atom escaping, and this is the local degradation. It may form cavities; it may lead to cracking; or, in some cases, swelling is also possible. So, these are some of the phenomena. If I want to present these words in a different manner, what will that be? You say damage to atomic and molecular structure causes changes in mechanical, physical, and chemical surface properties.

The formation of cavities leads to surface degradation, causing some materials to become brittle. We will cover a few examples of the conversion from ductile to brittle failure. When materials are exposed to radiation, atoms can migrate from inside to the surface or within the surface, resulting in reduced ductility and toughness, ultimately leading to cracking. In some cases, radiation exposure displaces and rearranges atoms.

That means we have intended something, we have designed some surface in some manner, and because of the radiation exposure to heat, these atoms are changing, and it happens most commonly in polymers and, in some cases, in the kind of rods we use, and then the swelling occurs, in this case only because of the rearrangement of atoms. As a result, the surface may be infected because of the swelling, and I guess some sort of rod coffin example has been cited as a nuclear fuel rod. They generally fail due to the swelling. Another one, as I mentioned, was the melting. I can say that melting is one of the most severe types of surface damage, which we also covered in the previous lecture.

It should be avoided. In that lecture also, I mentioned very clearly that it should be avoided as much as possible to limit the temperature rise. If you find that because of the circumstances, the temperature rises going on the higher side, we should make some arrangements for the cooling, and the cooling system must be employed and established to reduce the temperature. Now let us see some sort of heating effect on a microstructure. We see the effect of heating on a microstructure, and then we are showing a diagram in Figures 1, A, B, C, and D. Now here is some terminology: M, GB, PAGB, and martensite packets have been mentioned.

So, there is a need to expand, or maybe say that, and give a meaning to that. We say the GB stands for the granule bainite, M stands for the martensite, MA is a martensite austenite, and P is the grain boundary. PAGB is a prior austenite grain boundary, and in most of the steel cases, PAGB is very common; martensite is also common; and bainite is also common. So, we are trying to cover this, and then we say the nomenclature in this kind of microstructure. You are able to see that this kind of grain boundary here is shown as a red colour point.

Similarly, there is a martensite boundary in this case. This micrograph is at 40 μm , but when we zoom in, we can clearly see some boundaries and the martensite-austenite structure. These are grain boundaries and possible discontinuities in the material, indicating its constituents. If martensite dominates, brittleness will naturally increase. However, if the bainite content or its presence in the matrix increases, ductility will improve. This illustrates the reason for the change from bainite to martensite.

We say generally that after austenite, we try to go ahead with the heat treatment because austenite will not have a lot of hardness. We do a normalization, or normalizing, maybe air cooling, or we do a quenching also. So there are two processes. A and B are related to normalizing, and C and D are related to quenching. In the case of the quenching, we are finding the matrix of the martensite in greater detail, and even in this case, the PAGB is also there, but this one PAGB content may be 1, 2, 3, or 2, 4 martensite packets. So naturally, the hardness of the martensite will be on the higher side, but they will have much more chances of failure. How do we get this? Generally, we make a prediction well in advance using the CCT curve, which is a continuous cooling transformation curve.

What does it in this indicate? It indicates what the cooling rate is. Now if there is a temperature increase, maybe say 800 plus and we want to cool it. If the temperature decrease is very slow, then most of the austenite phase will remain there, ferrite will be in good shape, and then there will be ductile in the phase, or maybe failure will be ductile failure if it is subjected to a very heavy load. So, 0.1 degrees centigrade per second. Now coming to the water cooling, we go ahead with 100⁰ C/s or more than that.

Well, in this particular microstructure, which has been taken in this case, there is a roughly 340.5°C/s quenching effect under heat reduction, or we say that cooling is done in such a manner that the temperature comes down immediately or instantaneously. So this is changing the complete microstructure. The basic material is the same, steel; there is the same base material, but because of the normalizing heat treatment procedure, we are finding the structure is somewhat different. In the case of E and A, we are finding some sort of bainite formation, and in the case of C and D, martensite is dominating.

If you want to express in another word or maybe think in another word, what do we see? That is a prior austenite grain boundary that is a PAGB, which is important for understanding the microstructure scale of mechanical properties. Because of PAGB, if you are able to see it, you can really predict what the mechanical properties will be, what kind of strength will be there, ductility, fracture toughness, etcetera, and we can also predict the surface hardness. So it is important to understand what PAGB is, as in most of the steel cases it has been considered significant. Now coming to the normalized sample, we say that in the granule, bainite was the dominant, or we say that the GV microstructure with some sort of martensite may be less than the 5% we generally observe in this case, and if you look at the grain size, it will be roughly $25\text{ }\mu\text{m}$. This is slightly bigger than martensite because martensite micro is so small that the grain size will be roughly $24\text{ }\mu\text{m}$. However, in this case, also in granule bainite, we will find some sort of martensite austenite, but generally the size is very small, like less than $1\text{ }\mu\text{m}$, and they remain uniformly distributed. And then one main thing, particularly in granule bainite, is the lack of carbides, and that is a main reason why in martensite we find the many carbides.

In this case, carbide will be absent in a water-quenched sample. We find that the matrix is entirely martensitic with a slightly reduced grain size, around $24\text{ }\mu\text{m}$. The prior austenite grain boundary (PAGB) consists of 3 to 4 martensite packets. We also indicated a continuous cooling transformation curve, showing a comparison between water cooling and air cooling. Air cooling occurs at approximately 10 degrees per second (10°C/s), while water cooling occurs at around 340 degrees per second (340°C/s). The curve demonstrates that water cooling produces a completely martensitic microstructure due to the high cooling rate, whereas air cooling results in the formation of a granular bainite (GB) structure. The martensite formed after quenching has several dislocations, which increases the chances of brittle fracture.

To address the increased brittleness due to dislocations, we use thermal treatment, specifically tempering, to alter the microstructure. After initial water or air cooling, we follow the same tempering procedure for both cases. The aim is to understand whether the temperature changes the microstructure significantly, and this is what we explore through tempering.

Now we have already described PAGB in the prior slide, which was a prior austenite grain boundary. Either way, the two new terms are NT and QT. That is, we say the NT is normalized and tempered, and QT stands for quenched and tempered. So NT and QT will be utilized in this graph, and in this graph, micrographs A and B are related to the NT, and then C and D are related to the QT. What we are able to see in this case is that after tempering, we are able to see some sort of bulged boundaries and straight boundaries, and another one is that here the precipitation starts or carbide precipitation is also there, and this is what Zoom has shown: that here we are able to see in this case, after tempering we are able to see some sort of the bulged boundaries and straight boundaries, and another one is that here the precipitation starts or carbide precipitation is also there, and this is what zoom has been shown that here we are able to find coarse precipitation and then fine precipitation, but however the density of the this carbides is much lower compared to the martensite. This is where the density is very high, and moreover, in this case, we are finding

the coarse precipitates, while in this case the only and only the fine precipitates. We do not have a coarse one, so naturally, again, the hardness of this structure will be on the higher side compared to this structure. Because of this tempering, as we mentioned, there will be the formation of carbides, and then they will be involved with some sort of boundary, or maybe on the boundary, so that will change the microstructure and change the behavior of the surface.

So what we can say here is that the ferrite matrix is dominant in the case of the bainite structure. So a ferrite matrix with a straight and bulged boundary can be seen in this case, as I say, the bulged boundaries here and then straight boundaries, and this is magnified because this is a $5\text{ }\mu\text{m}$, this is a $20\text{ }\mu\text{m}$. So this is magnified, and then further, we are taking this as a sample, and further, we are magnifying it. So the magnified image shows a coarse carbide precipitation near the grain boundaries and fine precipitates throughout the matrix. However, again, they are not available and abundant, so we will find a much lesser density of these fine precipitates compared to the QT sample.

Coming to the QT sample, we say the ferrite matrix and carbides, which dominate in this carbide form the spherical discontinuities. There are some discontinuities available in this case and at the grain boundaries, and many more carbides compared to the anti-samples. So that is why we say that, most of the time, a QT-related sample with a quench and a temper will have a higher hardness compared to this. Now, if I really want to, then, from a property point of view, we should compare the properties. So what we are saying is the effect of the tempering on material properties. This graph has shown strain versus stress, and then we are indicating that strain in this case, particularly the blue color, is a QT that we are able to see is able to sustain higher stress. That means naturally the strength of a QT is on the higher side compared to the NT, but the elongation of the NT is on the higher side compared to the QT. Elongation can go up to this level, or maybe if you see the proportional level, that is a different thing, but otherwise it can be elongated maybe to 7 to 8 percent (7% to 8%), while this can be elongated to up to 15%, or maybe if you look at it this way, we can say it may be more than 10%.

In both tempering cases, we lose some elongation because the original austenite structure, which had an elongation up to 30%, undergoes heat and thermal treatment. This is significantly higher compared to bainite, normalized treatment (NT), or quenched and tempered (QT) structures.

The microstructure of the normalized treatment (NT) sample is predominantly ferrite with precipitate phases. In this case, there are both coarse and fine structures, along with discontinuities at the grain boundaries. If a load is applied rapidly, the NT sample may fail brittly, but with slow loading, it would fail ductilely.

In contrast, the QT sample has an abundance of carbides. These carbides are primarily distributed as spherical discontinuities at the grain boundaries. Unlike the NT sample, where carbides are dispersed within the grain boundaries, the carbides in the QT sample are mainly located at the borders above the boundaries.

So this is what the difference is when we are going through different thermal cycles; even though the base is the same, we can change the properties. And now why I have considered this as an example is because almost everybody has studied a steel and a steel formation, and we have also seen what the residual stresses will be at different levels and how the tempering is done to reduce those residual stresses. That is why this example has been mentioned, or maybe considered, because if we have a familiar example or we understand the familiar example, then we can relate. Now, if any material, let us say copper, is exposed to a high temperature or is exposed to high radiation, what will happen to those samples or to the polymers if they are exposed to the environment, which has a high temperature or even higher radiation? Now, what is the real meaning? Temperature and radiation both have a

energy, and whenever the energy is being given to the material naturally, it will atomic level and molecular level there will be some sort of change. Electrons will get energy, and then they will destabilize to stabilize back. They either need to leave some sort of ion, maybe some sort of atom, or maybe some electron, and that will change the structure or that will change the properties.

So that is why we have considered this initial example as a steel example or the steel formation, so that understanding about the temperature influence on the matter on related properties can be explained. Let us now come to radiation, and we often use the word photochemical degradation. The reason being that we are going to talk about photons, and whenever we talk about radiation, we generally express it in terms of photons, because photons are those that have high energy; we are not talking about lesser energy or negligible energy. So if a substance is exposed to UV or maybe other radiation, it will absorb photons, which increase the energy of molecules. Once the energy of a molecule increases, what happens to that? We know the stability, and then this curve has been picked up from reference, which has also been mentioned over here.

So, what is in this case, particularly this equilibrium point stabilized point? Now if a photon has been absorbed by this atom, then what will happen? This will get destabilized, and then it will leave, maybe whatever the critical part is, and then skip. So, this photon energy exceeds the escaping energy of the molecule or atom, and finally we lose those atoms. And it has been shown here that even if a high-energy neutron, or maybe radiation, has been imposed on the surface, we will be able to find some sort of dislocation or some sort of removal of the atoms from a matrix that will change the properties. So this is mentioned now. Here we are using the word photochemical. Sometimes we use the word photoionization. The same thing happens. We say the atom dislodges and creates a vacancy. This vacancy will continuously increase, and that will cause a void.

Radiation exposure is not just for a few seconds; it can last for minutes, hours, or even days. The longer the exposure, the more energy is absorbed, leading to increased material weakness and a higher likelihood of failure.

Radiation can dislodge atoms, creating vacancies and voids, and potentially breaking covalent bonds. Every covalent bond has a certain energy threshold, and if this is exceeded by additional energy, the bond breaks, altering the structure. When bonds break and vacancies are created, cracks can form. These cracks can grow under mechanical load, eventually leading to fatigue failure.

This concept also applies to polymers, which generally have low melting points. Even a small amount of energy, like a temperature increase to 200-250°C or exposure to radiation, can break bonds. This breakage can result in the formation of new bonds or cross-linking with other monomers, producing a weaker polymer compared to the original material. This process, known as photochemical degradation, ultimately reduces the strength and toughness of the polymer.

Another one is that a similar kind of process may also happen to some sorts of dyes and pigments. What is the meaning of that? Most of the time, you have seen that because of the sunlight, things change color, like, you know, maybe even the green color will fade slowly or maybe the yellow color will appear. So this is what we say: the change in the pigment happens also, or maybe a change in the color of the materials will happen, and then we need to really prevent it. We need some good coating on the surface. Another one that we have studied is something like photoionization, and then due to photoionization, there is a possibility of changing the electrical conductivity because we will be losing some atoms.

There will be some sort of effect on electrical conductivity, optical, or mechanical properties; those properties will change. And another important point is that instead of the UV, if we go ahead with the X-ray, then what will happen? X-rays will have high-energy photons that are effective in penetrating the material inside, induced ionization, and finally causing some sort of dislocation in the material. And in such cases, if it really happens to the metals because the metals are very susceptible to UV treatment, the brittleness will start. We will cover in this lecture a few examples of how brittleness will increase because of exposure to radiation. As the brittleness increases naturally, ductility will come down, which will also cause some sort of loss of strength in this case.

Now if you think about the non-metal itself, non-metals like glass or ceramic, because they have a high melting temperature, may not be affected that much by the radiation, or maybe a low temperature rise. However, if there is some sort of other polymer or the main thing is organic material, what will happen to the organic material if this radiation affects those materials severely? We need to study well in advance what will happen under different circumstances. So, either we should avoid those situations, or we should avoid those materials. Now we will come to a couple of examples and how they really affect radiation effects. So this is an example of the radiation effect on a metal and a non-metal.

This metal has been shown to be copper, and copper is very susceptible to damage due to radiation. You can see here that this is a microstructure; it is pretty smooth. While this microstructure has enough cracks in the boundaries, we are able to see, it is really impacted severely. So this is only exposure to radiation over a period of time, and this is common, particularly with copper. That is why we say radiation reduces the ductility of the copper. It increases the brittleness of the copper, and by dislodging atoms, they change the atom location and create a number of vacancies.

This is why we say that copper is subjected to embrittlement, meaning an increase in surface brittleness. Copper is typically a very ductile material, but exposure to radiation changes its microstructure, resulting in increased brittleness and the formation of numerous cracks. This occurs because radiation dislodges atoms, initiating cracks.

Regarding polymers, let's consider an example from a reference. When a polymer is exposed to radiation, discontinuities can form, and branches may be removed. In the presence of another monomer, new structures, known as grafted chains, can form. This process significantly alters the polymer's microstructure. Without radiation, the polymer maintains a stable structure, but upon exposure to radiation, the microstructure changes dramatically, affecting the polymer's overall behavior.

So these are the important aspects, and then let us explore a couple more examples. Polymer: now we are taking the example of epoxy. We say this is another good example, and it has been picked up from this literature. We are saying the UV radiation. You can see here the relatively smooth structure or microstructure at the beginning of the surface, which is what has been indicated in A1. Now if you keep for some time, maybe say around 250 hours, this is what we mentioned here. So if I keep this surface for the 250 hours, what will happen? We will be able to see some sort of nodule that is coming on the microstructure, which is also an indication of surface degradation.

If you extend the exposure time to something like 500 hours, you will see the formation of numerous cracks, indicated by the red color in the images. Similar to the copper surface exposed to radiation, the cracks increase significantly within this period. By 800 hours, the damage is extensive, with deepened cracks, and pieces can be removed from the material. However, as mentioned previously, it's important to keep the microstructure intact for proper analysis.

This significant damage to the epoxy, which has a relatively low melting temperature, occurs because radiation dislodges atoms, causing surface damage and changes in surface behavior. What was initially ductile failure transforms into brittle failure due to radiation exposure.

Additionally, the authors compared the material's properties over time. Initially, the tensile strength of the epoxy was around 29 MPa. After 250 hours, there was roughly a 5% decrease, and after 500 hours, there was a further decrease, although the bulk material still retained about two-thirds of its original strength. The toughness, initially around 26.24, dropped to roughly 20. This decline in toughness and shear strength, also known as pull-off strength, shows that all properties decrease over time due to radiation exposure.

So what we can mention here is that long-term exposure to radiation degrades the mechanical properties of epoxy. UV photons that are absorbed by the epoxy disrupt the chemical bonds, really excite the molecules, and generate free radicals. So that chemical activity will also be on the rise, and then it will cause more and more damage. So we need to keep in mind that UV radiation or maybe other kinds of radiation are really harmful for several materials. As I mentioned in a couple of examples, maybe ceramic or maybe glasses, there are a few materials that will not be affected by the radiation. Now let us cover a couple of more examples in this case, as you say that we are going to cover something like a stainless-steel example, and then the stainless steel changes behavior from ductile behaviour to brittle behaviour just by exposure to time and temperature. So this is the temperature and this is the time dependence, and then we are going to say that you know one covering a one example, which has been picked up from one of the references, what they did was they made a number of pieces or number of specimens, and then they exposed to the temperature of 475° , which is a high temperature, and then what is not a lesser the melting temperature of the stainless steel.

When they examined the microstructure, they found one sample that was fractured after being exposed to 475°C . The fracture was observed immediately after two hours of exposure, showing deep dimples in the microstructure, which indicates a ductile fracture. A similar experiment was conducted after four hours of exposure at the same temperature. The sample was prepared, fractured, and examined, revealing deep dimples, though with slightly lower density than after two hours, still indicative of a ductile fracture.

In both cases, the deep dimples observed in the microstructure indicate ductile failure. However, when the sample was exposed to 475°C for eight hours, the subsequent fracture revealed dimples and ridge formations, suggesting the initiation of brittle failure. After 16 hours of exposure, the microstructure showed a significant reduction in dimple density and the presence of a river pattern, which is characteristic of brittle failure.

Of course, after 32 hours and maybe 64 hours, we are able to see many, many cleavage failures. In this case, cleavage failures are there, and that is indicative of what we call brittle failure. So this basically highlights that there is a relation between the embrittlement and microstructure as brittleness increases because of the time, even though in all six cases the temperature is the same 475° exposure was for 2 hours, 4 hours, 8 hours, 16 hours, 32 hours, and 64 hours. In this case, the brittleness—we say the brittleness—is continuously increasing, and then this has the highest brittleness. So this is important to consider if you are and whatever the temperature you want, but how much time the temperature environment remains for the sample. If it remains for 2 hours, 4 hours, 8 hours, or 16 hours, naturally, material behavior will be different; even the surface that you are going to get after the fracture will be different, and that is the topic of how the fracture will change with time, how the fracture will change with temperature, and how the fracture will change with radiation.

Now they have also published in the hardness curve what has been mentioned here. This is what we are using for the word aging time: the same thing in the number of hours instead of that, now they have put in the number of minutes, and then they measure the hardness also. We are saying that as age is the same, the sample is kept for more and more time, and interestingly, their hardness is increasing. I assume initially that hardness should come down with the high temperature, and with a certain amount of time, it should decrease because the creep behavior indicates that there will be more and more chances of failure. But here we are talking about the hardness, and then they have plotted that the hardness will increase.

Now they have also given justification, or they say the age significantly enhances the hardness of ferrite. So there are two: maybe stainless steel has ferrite, and austenite does not. So austenite keeps harnessing, while ferrite hardness is continuously increasing. As the ferrite hardness continuously increases, embrittlement happens or embrittleness increases, and then the chances of brittle failure will increase. So what we can see with the time is that the is that the ferrite phase becomes more and more fragile, more and more prone to brittle failure, and then, as we have mentioned here, it shifts the microstructure from failure; the microstructure of the felt sample or surface shows a lesser dimple with the time, which is the shift from a dimple to the tearing rupture that happens in this model.

Our aim was to introduce this topic and demonstrate how temperature and radiation affect materials. Except for a few materials, the majority are significantly impacted by temperature and radiation. I noted that we can analyze these effects individually or together, with the combined effects being more severe and dominant than the individual ones.

This concludes our current lecture. Next, we will begin discussing corrosion, which is an extensive and critical topic. We will explore how corrosion affects surface degradation and how it influences adhesion, abrasion, and fatigue. These subjects will be covered in the upcoming lectures. Thank you for your attention.