Nature and Properties of Materials Professor Bishak Bhattacharya Department of Mechanical Engineering Indian Institute of Technology Kanpur Lecture 13 Metals 3

Okay, today we are going to talk about strengthening and corrosion in metals, so we have gone through various types of metals and metallic alloys. And we have already seen that the alloys are created with an intention to actually improve the properties of a metal. So there are some basic techniques towards this, which I will be talking about when I will discuss about the strengthening of metals.

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Now also because of the basic metallic nature, there is there are always susceptibilities to different kinds of corrosive environments, so that also we will talk in this $2nd$ section of it. So both strengthening and corrosion of metals in what we are going to discuss today okay. So strengthening mechanism in metals, corrosion in metals and some of the corrosion types and their prevention, this is what our object of study today.

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Now, $1st$ of all the strengthening mechanism in metals. One thing we have already seen that dislocation if it is present in a metal, then it actually degrades the material properties. Now, as long as the dislocation is actually limited inside a particular grain, there is no problem in the sense that the macroscopic properties will not be that much affected.

But if there are many grains which gets affected by dislocation all adjacent grains, then actually that would substantially affect the mechanical properties. So the ability of a metal to plastically deform depends on the ability to dislocate and these dislocations to move across the grains. And if we can stop this movement across the grains, then you can make a material harder and stronger.

And there are several ways by which you can do it, one is through the grain size reduction, then the other one is solid solutions strengthening and then of course then strain hardening, then there is precipitation hardening, et cetera. So let us try to look on some of them one by one. So $1st$ of all, we discuss about the grain size reduction.

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Now, the grain boundary acts as a barrier for dislocations that we have just now said, but how does it acts as a barrier for dislocation? There are 2 reasons by which it can happen. One is that there is the miss-orientation that means if to grains are there and these 2 grains are not oriented, their lattice are not oriented then it will be difficult for a dislocation to pass into another grain okay, so if there is a loss of alignment between the lattice structure of 2 grains okay.

So suppose in this particular example you consider this to be one grain and then you have this one, the 2 lattices are not aligned okay, so there is an angle. So then it will be difficult for dislocation to move from this to the next lattice, so that is what is called miss-orientation. Now you imagine that in terms of number of grains in a particular surface area.

If you have more and more and more of these grains okay, which is oriented with respect to each other, then it will be more and more difficult for the dislocation to effect all of them in a kind of a statistical scale, so the more it will face these grains the more difficult it will be for the dislocation to pass. So that is one of the reasons why smaller grains that mean more grain boundaries would actually stop the dislocations very effectively to move across the grain boundaries.

The $2nd$ one is the atomic disorder because near or within a grain boundary region, this atomic disorder generally leads to a discontinuity of slip planes from one grain to the other, so that is also another possibility where the dislocation should not be able to move.

There is also another $3rd$ possibility that means and it is actually more it starts not with the dislocations, but with the point defects that a inside a grain the probability of having a point defect at a particular point is not the same in the next grain. So as a result, the piling up of this kind of defects or dislocations that is not possible uniformly across all the grains.

So if there are more number of grains, the less the probability that dislocation pile has occurred in all of them at the same uniform rate and hence the dislocation movements would be lesser and lesser. Now, a fine grain material is then harder and stronger than a coarse grain material and due to as I said that the great the larger grain boundary area to restrict the dislocation motion.

This was 1st observed by Hall in University of Sheffield close to 1950s Hall has observed this first in steel alloys and later independently Petch has also observed the same not for steel alloys, but for other alloys. So what Hall noticed is that the relationship between the yield strength and the average diameter D actually follows this kind of nonlinear relationship between the average grain diameter and Yield strength.

And there are 2 constants, sigma 0 and K y, which govern this relationships okay. Interestingly, that is the same thing Petch has later on seen that it is not only for mild steel, but for other materials also the same thing happens.

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And people have found out through experiments the values of this Hall-Petch constants like for Copper it is sigma 0 is 25MPa and the K is about 0.11MPa meter to the power half. For Titanium, it is 80, 0.4, Mild Steel 70, 0.74, Ni3Al it is 300 and 1.7. Now, one important thing is that it is the K, which actually kind of determines that how much of the effect of D will be on the overall sigma Y okay.

So suppose if I consider the mild steel okay and I have to configure here the diameter of the grain from about 100 nanometre to about 1000 nanometre and I have considered these values of sigma 0 and K as 0.74, which means sigma Y is actually $70 + 0.74$ D to the power - half.

And then I have given all these values okay, so we can really see yes that the sigma Y as the grain size is increasing okay. It will go not at a very high level, but it will indeed decrease in sigma Y. So the Hall-Pitch constant very nicely describes how the mild steel is actually the grain size affects the strength of mild steel and similarly for the other alloys.

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Now, let us talk about another form of strengthening okay so that is known as the Solid solution strengthening. So in this case the strengthening is occurring because there are few know so called pinning of the impurities okay inside the grain and which actually stops the growth of the dislocation or the dislocation piling. So in fact, you would see that pure metals that is why are almost always softer than their alloys

Why, because these alloys I have talked earlier about for example these substitution of alloy atoms, right the alloy atoms in a solid solution right in the interstitial spaces for example. So whenever these impurities go in the interstitial or substitutional position, then what happens? Either if they are actually the atoms are actually on the host atoms of the atoms that goes inside if they are larger in size, then there will be a compressive strength which will be developed in it.

And on the other hand, tensile strength will be imposed on host atoms by smaller impurity atoms. For larger size of atoms will give a compressive strength because it is taking more space, so it is actually pushing all the other atoms inside the grain, so there is a compressive strength. And if you put a smaller one, then others are also coming towards it and as a result there is a tensile strength.

In both the cases thus, you can actually influence the dislocation stress, which is actually denoted by the Burger's vector, so you can influence it with the help of the impurities. So thus basically the impurities actually can anchor very effectively with dislocations and that is why alloys are generally much longer than pure metals. Like you can consider Nickel weight percentage okay.

And as you can see that here the tensile strength as the Nickel alloying is increasing in copper, you see the tensile strength is actually increasing. And also its elongation is decreasing because it is becoming harder and harder okay. So that is another strategy of making materials the pure metals harder by inserting impurities. Now we will talk about Strain hardening.

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Now Strain hardening is so in the other cases you are actually playing with what you call the grain structure, but here you are not doing that. You are actually using a mechanism in such a manner that you are applying the work hardening or cold working okay, so that there is a strain that you are imposing on the nearby atoms inside the grain structure and thus you are really actually increasing the strength of the material.

Now, that strain increases the so called the strength that you must have seen in the stress strain diagram itself, when beyond a certain percentage of strain there is a strain hardening area that occurs okay. So the idea is very much similar but in the formation of the metal itself, this particular technique is thus used and the hardening happens to the system.

And there are for example, you can see here that percentage of Cold Work okay, how it is changing the strength okay. While increasing the strength, how you are actually strength is increasing, but the ductility is actually sacrificed in this process. And you can actually measure the percentage of cold working if you know the original area and the deformed area and you know how much percentage of cold working has taken place.

And if there are readymade charts available from which that how much of strength increases, you can expect from the strain hardening. Now the strength that is increased can sometimes is controlled also by actually annealing. So that is what is actually a heat treatment process okay through a slow heating and slow cooling you can actually release some of it okay and thus you can control, you can bring a trade of pollution between the strength and the ductility of a system.

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So far we have discussed 3 methods right. One is the refining of the grain boundaries as these grain boundaries serves as barrier to dislocation motions, so by having a more refined polycrystalline material, you can increase the strength. Of course, there is a degree up to which you can do it. In fact, later on it is called reverse Hall-Pitch perfect that people found out that if you reduce the grain structure beyond a certain level okay, then this becomes counterproductive.

And so it actually depends on the side of the dislocation okay. If the opposite side of the dislocation is 10 nanometre and if you are bringing a grain structure of a similar level, then the dislocations it will not be difficult for the dislocations to actually get piled up across the grains anymore and hence, instead of increase of the strength you may see the decrease of the strength, so the reverse effect may happen if you reduce the grains too much. So there is an optimal level of grain size for every metallic system.

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Then the $2nd$ way of doing it is of course solid solution strengthening, which is with the addition of the impurity. And as we have shown you earlier that both of these Solid solution strengthening and Strain hardening, they saw there are so there are these 2 counter objectives that while adding impurity or while increasing the percentage of cold work, you are actually strengthening the system, but you are sacrificing the ductility, so you have to take a rational decision towards it.

There is another effect which is considered in many industries that is very popularly known as Precipitation or Age hardening. So what is done in this case is so far temperature is not really considered in this entire scenario but you will bring temperature than actually the phase boundaries come into picture because every impurity, their solubility changes a as you are changing the temperature.

So based on the changes in solid solubility with temperature, you can actually produce fine particles of an impurity phase and which can block the movement of dislocation. So suppose at a slightly higher temperature you may see that there can be more impurities that can be spread over inside a pure metal and the act like the nucleation points and then as keep it at a very low cooling rate.

Gradually what happens is that these impurities actually affect the grain formation and as well as it affects the hardening. So these temperature and to change the solubility and later on allowing more time for the grains growth actually is known as the ageing. So Precipitation Age hardening, these 2 things actually go hand-in-hand. This is another mechanism in terms of controlling the hardening okay of a pure metal.

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Now these are so far whatever we have discussed are related to the improvement of the metal. however, metals also suffer from a problem, the ceramics will not suffer from it that they get corroded okay. I have talked about it you know in the very beginning if you remember I have shown you the periodic table and I have shown you the relative positions of the metals okay that they have tendency to give away the electrons okay.

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So as a result of this tendency, they can easily actually react with the environment and those inorganic materials, which can absorb these electrons they can quickly react with these metals and this results in corrosion. And these corrosions are definitely destructive, they are unintentional attack on structures and they are basically electrochemical in nature.

You can see corrosion of a ship or a automobile or a pipeline in every case corrosion creates a severe problem. Now the material loss that takes place can be either through the solution or through formation of scale or live film okay. So that means the reaction takes place and the compound actually forms over the surface like a film or a thin scale.

For example, you take an Aluminium vessel okay and you put water in it and when you try to eat it up and you do this for several times, you gradually see that there will be a layer of Aluminium oxide which will be formed on Aluminium at a higher temperature and that will come like a green sheet for the Aluminium, so like a thin scale or film.

There are various ways in which this takes place and there is approximately 5% even higher in some cases of a industrialized nation's income which is generally spent for the corrosion prevention, maintenance, et cetera, so that means it as a big issue for various systems.

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Now there are 2 parts of this kind of chemical corrosions; one is the oxidation reaction or Anodic reaction. In this case, this is related to the tendency of the metals to actually give up the free electrons and the other is the cathodic part, which is just the opposite part of it where electrons are transferred to another chemical species based on their position in the periodic table that they will be able to accept electrons.

For example, Zinc okay so Zinc can readily give up 2 electrons and this can be taken up by hydrogen and hence the moment you keep Zinc, there will be a Zinc convert it to Zinc ion and Hydrogen gas will be formed. In fact, many a times that is why Zinc is given as a sacrificial layer coating so that make that very readily react and save the metal, so I I will talk about it that what is the significance of this type of layer.

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Now, when we select as a result such material to provide a protective layer over the original material, there is something called as a Piling-Bedworth ratio PB okay, which is nothing but the volume of the oxide that is forming during reaction to the volume of metal that is consumed in the oxidation, so if suppose the PB ratio is greater than 2, what does it mean?

It means lots of oxides are getting formed and relatively less amount of metal is consumed in the oxidation okay. So as a result what will happen is that there will be high compressive stresses in the oxide film and because the volume of oxide formed is quite high and there will be oxide cracks and flaking off and this material then cannot be used as a protective material because of its tendency to develop cracks and flaking off.

If PB ratio is less than 1, that will mean that the volume of oxide formation is smaller in terms with respect to the volume of metal consumed and that will create another type of trouble, where actually tensile stress will be generated in the oxide film and hence, there will be brittle oxide cracks and thus un protective, so this is the case where the PB ratio is less than 1 and this is the case when PB ratio is greater than 2.

So there is this flaking off as you can see that flaking off is taking place, the layer will come out. So if the PB ratio is between 1 and 2, then actually it will very nice sits on the base material, so it works very nicely as a protective coating. So for example, if you use a Potassium as earlier, Potassium oxide will form that the PB ratio is much less than unity, so that means that there will be brittle oxide cracks and Potassium cannot be used as a layer.

If you use Sodium, 0.58 the same problem okay, there will be cracks due to tensile stress. Magnesium oxide again similar problem, but Aluminium oxide it is between 1 and 2, so it will very nicely work like a protective coating that is why Aluminium oxide layer is used in many cases as a good protective layer and Aluminium itself is also is much better in terms of corrosion because a part of Aluminium is sacrificed for Aluminium oxide formation and that gives nice coating on the pure Aluminium.

Um then there is the other ones, which are gradually going like Chromium is possibly last one, beyond Chromium it is greater than 2 and hence you cannot use it as a protective material. So thus PB ratio works like a nice guidance in terms of choice of the material. The other point is the reactivity of a metal in seawater okay particularly for sea work the vehicle, this is very important.

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So susceptibility for corrosions in sea water that reduces if you go from the upward journey, so you consider Monel. Monel is very heavily used today for all nuclear power plants, where actually the sea side nuclear power plants where Monel is used. It is because of its high capacity for anticorrosion and we already said that the advantage of Nickel on copper in terms of the high strength.

So both from corrosions as well as from strength point of view, Monel is an excellent material. And the Inconel also is another one in fact, the secret of making this material is very very industrially significant, not many nations would like to (())(26:24) with this state secret. And then you have Stainless Steel, Titanium, Graphite, Gold and Platinum of course are even better, but you cannot use them.

Um In terms of the susceptibility what you will be very much conscious about is like using Iron okay and also Aluminium alloy Cadmium, Zinc is highly susceptible we have seen. So thus Galvanic series gives us a good guidance in terms of the reactivity of metals in the seawater. Now the corrosions are generally of 2 types.

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One is the so called Uniform atom corrosion is the most common form of corrosion as you can see this is a jetty where this anchoring positions are getting uniformly attacked because of the salty conditions and the oxidation reduction reactions occur randomly all over the surface and there is a maximum metal loss that occurs in this kind of uniform atom.

The other one which is known as Galvanic corrosion. This is very specific case where actually the different types of metals are used for joining or doing some work like a junction of 2 different types of metals okay, like say Copper-Steel junction okay. Now, this kind of thing happens in boilers.

For example, it happens in various types of for example aircraft these wiring of the aircraft system, they actually wherever you are actually anchoring this works, those are actually junction when there also this dissimilar metals will be galvanic series, they actually come in close contact with each other due to mechanical actions.

And then the moment that happens, there will be a kind of a cell formation, so one would act like a cathode and the another would work like anode and as the result, there will be continuous corrosion of materials from one to the other, so this is something which is galvanic corrosion, this happens because of very specific applications where dissimilar metals or materials are in contact with each other.

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Then there are Inter-granular corrosion, this occurs along the grain boundaries in some of the alloys like stainless steel at a high temperatures for a long time if you keep it, what will happen is for example, in steel heat causes the formation of Chromium carbide particles along the grain boundary and then this will create corrosions along the grain itself.

And hence this kind of things is particularly very important when this type of hightemperature for a long time kind of situation comes into picture particularly for turbine blades and things like that. Then there is this stress corrosion, now stress and corrosions, stress corrosion is places where you have a high level of stress as well as you have corrosions due to chemical kind of results.

So here, high stress (())(30:03) the problem okay because the material gets weaker and there will be more or larger surface which will be exposed and as a result the 2 things actually help each other to increase the corrosions process. The other one is would be erosion corrosion process, which is a combined effect of chemical attack and mechanical wear due to some kind of fluid motion for example, propellers, turbine blades, valves and pumps okay.

Even in pipelines where there is this if there are some of the abrasive particles if the pipeline carries, then there will be erosion as well as the corrosion, so there is a combination of wear and corrosion. So either stress or corrosion, wear and corrosions these are the kinds of you get in severe condition so it is not only corrosion, but also something more than that that affects the system.

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Then there is Crevice corrosion, it is actually a localised corrosion occurs due to concentration difference of fluid ions between 2 regions of the same metals as okay, so concentration difference of fluid leads to corrosion. And Pitting corrosion and like small pits and hole formation, it it generally initiates by scratch on surface and then it goes downward due to gravity, so these are various forms of corrosions that are possible in a system.

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Now in terms of corrosion resistant Aerated water, this type of material so you see the environment which is important like Lead alloy, Steel alloy, Titanium alloy, Nickel alloy, Copper alloy, all of them gives high resistance. But Aluminium alloy low, low resistance particularly in Carbon steel. Strong acidic or medium if it is, then you see we will see Titanium alloy or Lead alloy or stainless steel, Aluminium alloy is medium.

If it is strong Alkaline, Nickel alloys, Steel and Titanium alloy. Medium is Copper alloy and Zinc alloy and UV generally all alloys. So one common thing that we can see is that no matter whatever is the medium, Titanium alloy is actually good in most of the corrosive environments, so that is why they are heavily used for corrosive environment. There are certain strategies for corrosions prevention.

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One is that of course use material which of course based on PB ratio, which can form a good protective oxide layer. Other is, add inhibitors for example, Amines and hydrazine, which can remove the oxygen because oxygen creates most of the corrosions, so use some such inhibitors. Another is, reduce temperature because we have seen that at high temperature corrosion increases, so reduce the temperature decrease the corrosions rate.

Apply paintings, chemical painting or go for Cathodic protection like metal to be protected is connected to another more reactive metal, which gives up its electrons and get readily oxidized in a sacrificial anode and this is why people use to actually carry Zinc okay in the ships earlier days because then the Zinc will be oxidized, Zinc will be sacrificed but the ship metal will be saved. Magnesium and Zinc are more commonly used for this type of purposes.

So these are the various methods for corrosions prevention. This is where we will come to an end and in the next lecture we will talk about ceramic material, their classification and crystal structure, thank you.