Friction and Wear of Materials: Principles and Case Studies

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Lecture – 08
Wear Mechanisms:
Tribochemical Wear and Oxidative Wear

Welcome back. In continuation of understanding several wear mechanisms, today we will learn about tribochemical wear and the oxidative wear mechanisms.

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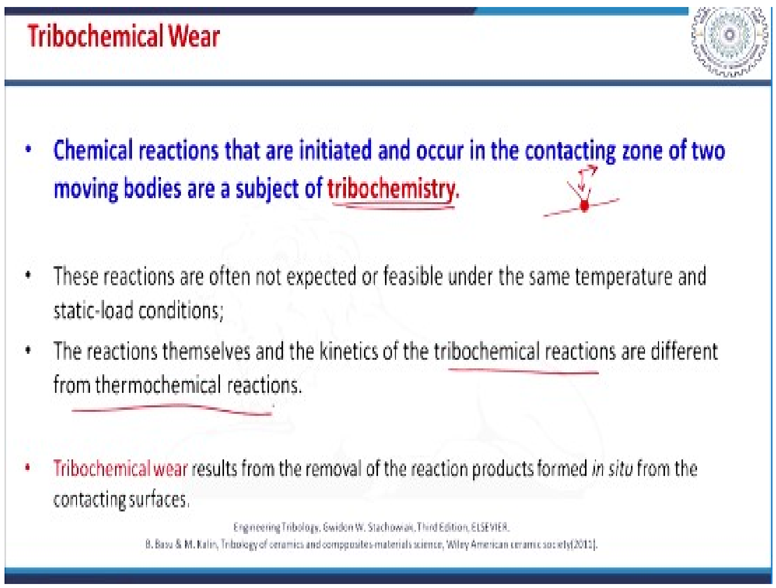

Generally, chemical reactions that are initiated and occur in the contacting zone of two moving bodies are a subject of tribochemistry. what is that you mean by tribochemistry? When you have two bodies moving relatively and there are in contact, so there can be a reaction happening at that contact but they are subjected to the sliding conditions or wear conditions.

What happens? There is a synergistic effect of these mechanical wear at the same time, the chemistry also plays an important role. So, you will have a synergistic effect of this chemistry as well as this mechanical wear. You have the tribochemistry playing a role in material removal that we called tribochemical wear. These chemical reactions are often not expected or feasible under the same temperature and static loading condition.

Whereas, this dynamic loading conditions even lesser temperatures are sufficient to trigger such reactions at the contacts because of the stimulated contacts and the high stress conditions at the contacts. There are reactions themselves and the kinetics of this tribochemical reactions are different from normally observed thermochemical reactions. So, tribochemical reactions are different from thermochemical reactions with respect to their kinetics.

The material removal due to such involvement of tribochemistry at the contact is called tribochemical wear. So, the tribochemical wear results from the removal of reaction products formed in-situ from the contacting surfaces. You will have several examples of such instances of tribochemical wear.

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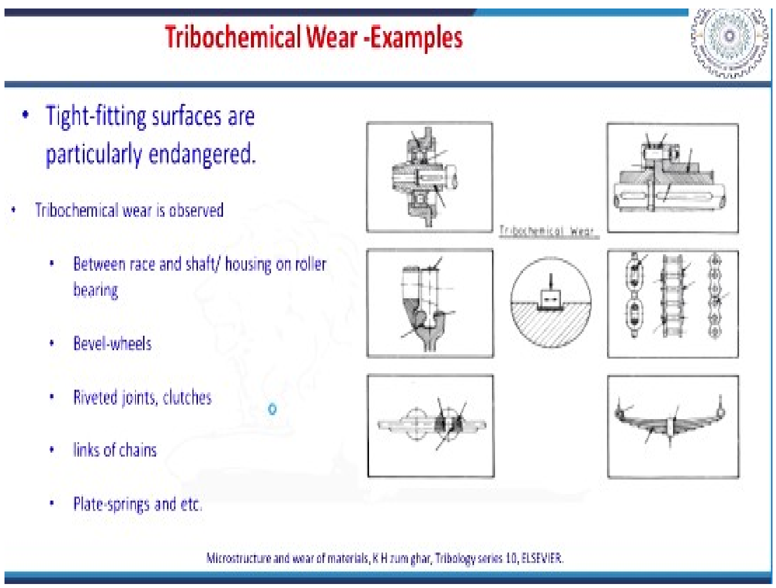

So, tribochemical wear is observed generally between race and shaft on roller bearings, or bevel wheels or riveted joints, clutches, links of chains, plate springs etc. There are several examples where the tribochemical wear dominates in material removal.

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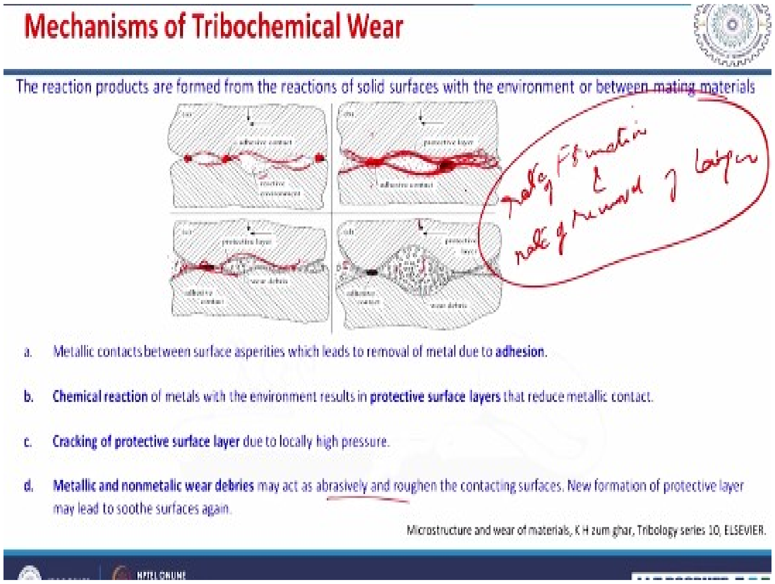

So, we need to understand the micro mechanisms involved in such material removal. As I told the material removal is a synergistic effect of that rubbing action as well as the chemistry or the chemical reaction products. The reaction products are formed from the reactions of solid surfaces with the environment or between the mating materials. For example, you see here for a metallic material system, the metallic contacts between the surface asperities, you can see there are contacts at the surface asperities that leads to material removal mainly because of the adhesion.

The material removal at this contact is because of their adhesion, that this is adhesive contact. So, the chemical reaction of metals with the environment results into these protective surface layers. Layers that now reduce the metallic contact. So, what is happening? Because of the reaction, layers are in between these two contacts. So, you will have reduced metal to metal contacts.

But how the material is removed? Material is removed by cracking of this protective surface layer because of the high pressure. So, what happens? There is debris forming out. The metallic or non-metallic wear debris may act as abrasive particles and roughen the contacting surfaces. So, the new formation of protective layer may lead to again soothe the surface. So, it is a continuous process.

So, the wear debris comes and then again contacts. So, wear debris comes out again. So, it is a continuous process of first making an asperity-asperity contact become giving rise to adhesion and then there because of the reaction with the environment of this metallic surfaces, they will have the protective layers. But as the pressure is increased at the contacts, the layers are broken and the material is removed as a debris.

Again, there is a protection layer. So, it is a continuous formation of a layer and continuous removal of this layer. So, they actually contribute to the tribochemical wear. So, the rate of formation or the rate of removal of this layer actually dictates whether the tribochemical wear is beneficial or not. If the rate of formation of this tribochemical layer is more than the rate of removal of this layer, then you have a protective surface. So, the wear is reduced.

If you have the rate of removal more than the formation, you have material removal continuously. So, you will have a more amount of material removal. So, the tribochemical wear is not beneficial or the formation of such tribochemical layer is not protective.

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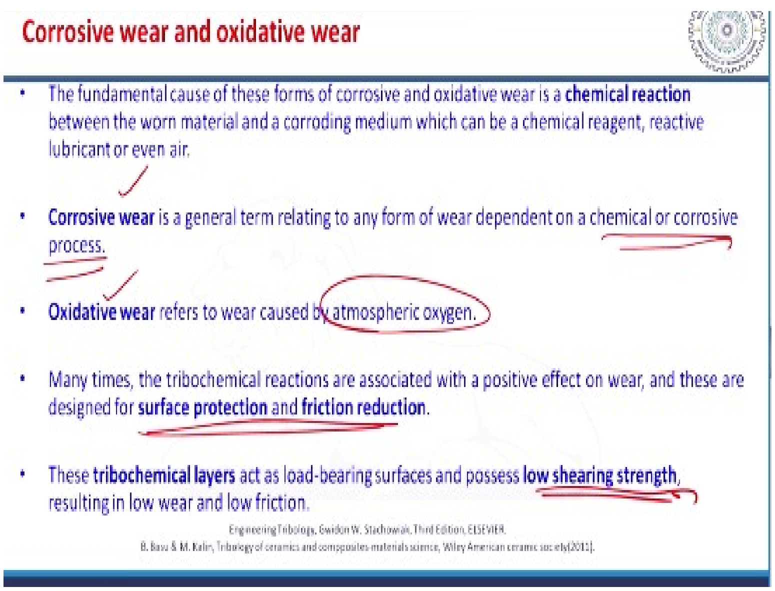

The fundamental cause of these forms of corrosive and oxidative wear is a chemical reaction between the worn material and a corroding medium which can be a chemical reagent or reactive lubricant or even in air. So, you can also say this corrosive wear and oxidative wear are synonymous for this tribochemical wear, only their kinetics are different. we will also try to understand this corrosive wear and oxidative wear in this class.

Corrosive wear is generally a term relating to a any form of wear depending on the chemical or corrosive process. So, you will must have a chemical or a corrosive process that leads to corrosive wear.

Whereas, oxidative wear refers to wear caused by the atmospheric oxygen. So, the wear happens in atmospheric ambient conditions, then we call oxidative wear. If it happens in chemical or corrosive conditions, we call it as a corrosive wear. Many times, the tribochemical reactions are associated with a positive effect on wear and these are designed for surface protection and friction reduction.

But as I told, they can be detrimental to certain conditions as well. We will also study several example case studies where we will see the beneficial effect of tribochemical wear or detrimental effect of tribochemical wear for different classes of materials in different conditions of wear, right. These tribochemical layers act as load-bearing surfaces and possesses low shearing strength resulting in a low friction and the low wear.

So, if the layer has a less shearing strength, it will be easy to slide. So, you will not have a friction increase, or the material removal can be subsequently reduced.

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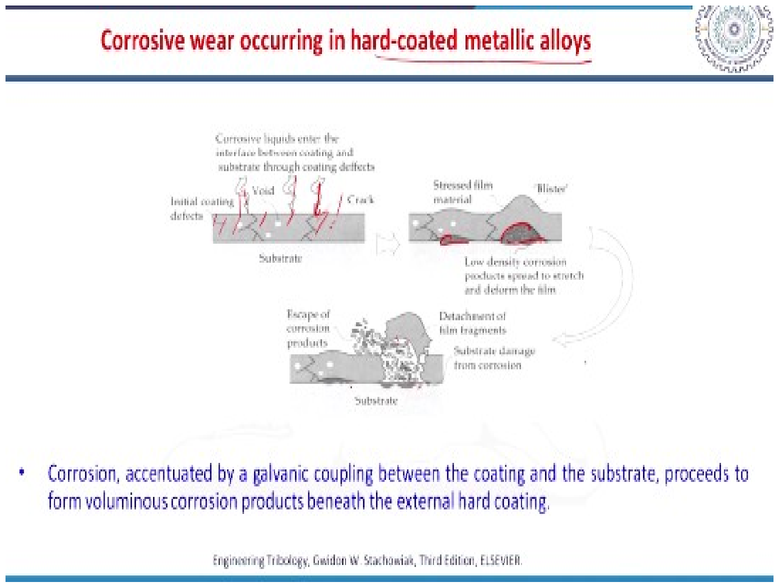

So, the corrosion is accentuated by galvanic coupling between the coating and the substrate that proceeds to form corrosion products material removal beneath the external hard coating. If you see the corrosive wear occurring in hard-coated metallic alloys, initially you have this coating. Corrosive liquids enter the interface between the coating and substrate through several material defects.

When it enters into, then you will have corrosion products. That corrosion products being a less in the density, they easily spread. Because of the easy spreading of these, this coating is stretched and even deformed, and it may even lead to fracture. So, the detachment of these coating comes out and then substrate damage leads to the corrosion increase. So, you will have a corrosion accentuated by galvanic coupling between the coating and the substrate proceeds to form voluminous corrosion products beneath the external hard coating.

So, corrosive wear is one of the important wear mechanisms that occur in the metallic alloys coated by hard materials in corrosive conditions.

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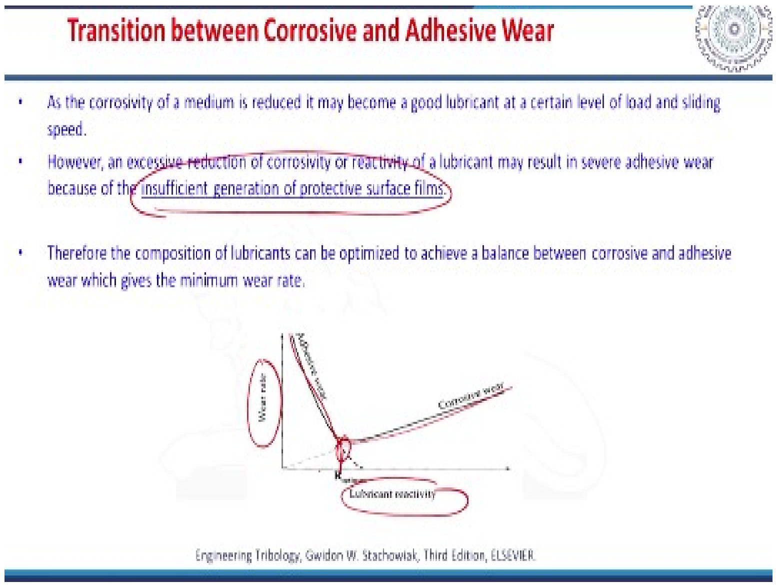

So, there happens always a transition between a corrosive in adhesive wear. As the corrosivity of the medium is reduced, it may become a good lubricant at a certain level of loading and sliding speed. But however, an excessive reduction of the corrosivity or reactivity of a lubricant may result in severe adhesive wear, because of the insufficient generation of protective surface films.

So, you can see the wear rate versus the lubricant reactivity. Adhesive wear is dominant up to this and then corrosive wear is dominant. So, there happens certain reactivity optimum where you can have both adhesive and corrosive wear at the minimum levels. The composition of lubricant has to be optimised to achieve such a balance between the corrosive wear and adhesive wear which gives the minimum wear rate.

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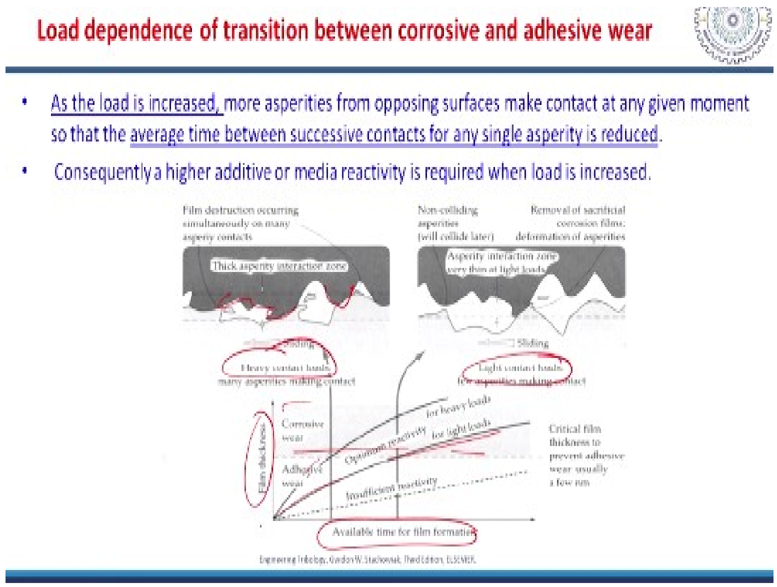

As the load is increased, you will have a transition between the corrosive to adhesive wear. So, as the load is changed, you have a transition between the corrosive and adhesive wear. Let us see here the loading conditions and high loading conditions, we will have a light contact loads and heavy contacts loads. As the load is increased, you see the film thickness and the available time for the film formation.

You will have adhesive wear and then the corrosive wear. As the load is increased, you will have more asperities from the opposing surface that come in contact at giving movement. So that average time between the successive contacts for any single asperity is reduced. So, you will have a higher additive or the media reactivity required when the load is increased.

You will have again a transition when the load is changed. So, as the load is changed, you will have a transition from corrosive and to adhesive wear, right.

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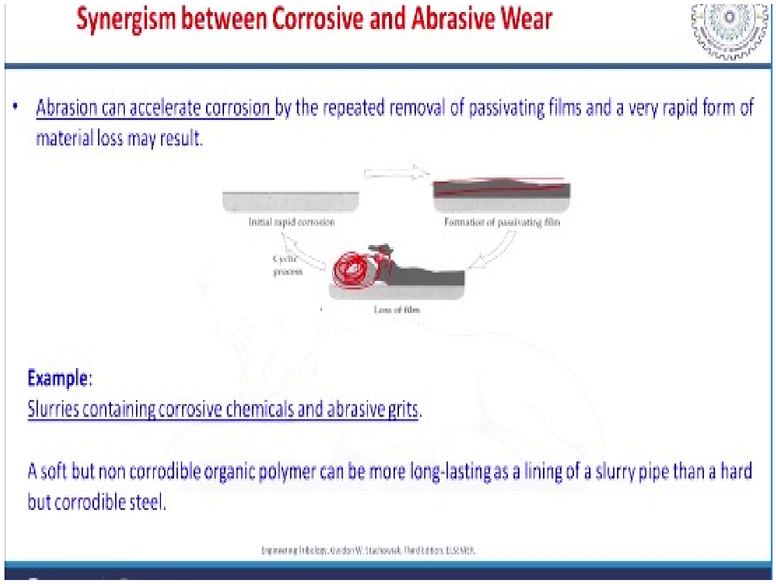

The material removal in such corrosive conditions in abrasive wear stress conditions is because of the synergetic effect of this corrosive and abrasive wear. You see here, initial rapid corrosion you will have a film and because of this abrasive coming hard grit or hard asperity come in contact, this film will be broken. And then again, the cyclic process proceeds with the corrosion, but now very rapid rate of corrosion.

And then again, material forms as a passive film again material removed. So, it is a continuous process of abrasion, they actually accelerate the corrosion by the repeated removal of passivating films, and a very repeated form of material loss may result. So, you can find such synergetic effect of corrosive and abrasive wear in slurries containing corrosive chemicals and abrasive grits. A soft but non-corrodible organic polymer can be more long lasting as a lining of a slurry pipe than a hard but corrodible steel.

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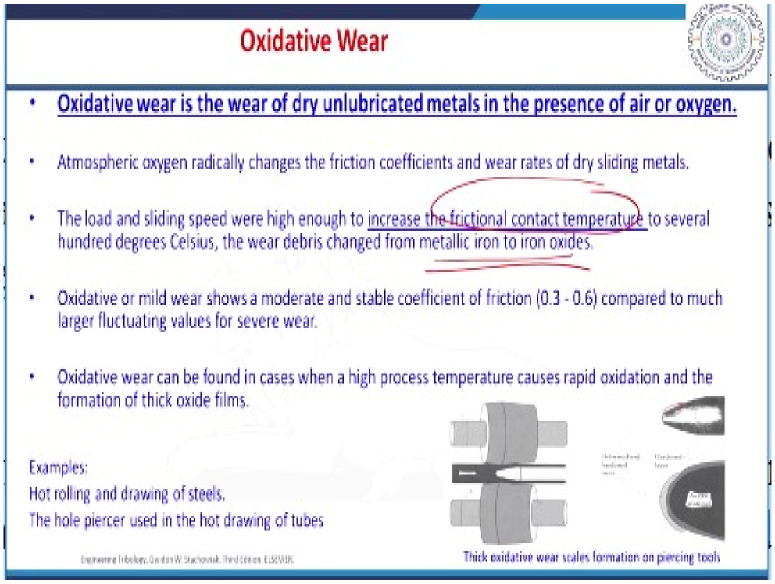

Oxidative wear is a wear of dry un-lubricated materials in the presence of air or oxygen. So, atmospheric oxygen radically changes the friction and wear rates of the dry sliding materials. If the parameters of the sliding such as loading and sliding speed are high enough, then they increase the frictional contact temperature to several hundreds of degrees of Celsius.

Then, the wear debris changed from metal to metal oxides. So, you will see several examples where such metal becomes metal oxides in such high contact temperature conditions, because of the friction. Oxidative wear or mild wear shows a moderate and stable coefficient of friction compared to much larger fluctuating values for severe wear. Oxidative wear can be found in cases when high process temperatures causes rapid oxidation, and the formation of thick oxide films will have a more amount of material removal by this oxidative layer removal.

So, examples you can see hot rolling and drying of the steels; All the hole piercer used in hot drawing of the tubes; You can see thick oxidative wear scales formation on the piercing tools. You will have material removal mainly because of the oxidative wear.

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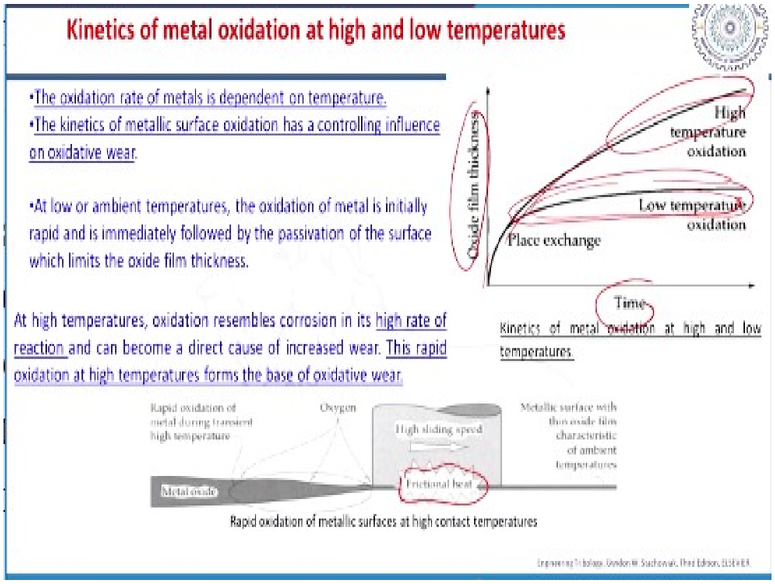

As I told the kinetics of this tribochemical reactions are different. So, the kinetics of metal oxidation are dependent on the temperatures as well as the stresses. The oxidation rate of metals is dependent on temperature. The kinetics of metallic surface oxidation has a controlling influence on the oxidative wear. If you look at the kinetics of metal oxidation high and low temperatures, at low or ambient temperature the oxidation of metal is initially rapid followed by passivation of the surface which limits the oxidation film thickness.

Yoy can see the oxide film versus the time, initially there is a low temperature oxidation and then the high temperature oxidation. At low or ambient temperatures of oxidation, the oxidation of metal is initially rapid followed by the passivation of the surface which limits the oxide film thickness. You will have a lesser film thickness in lower temperature oxidation. But at high-temperature oxidation, oxidation resembles almost corrosion in its high rate of reaction and then become a direct cause of increased wear.

So, you can have an oxide film thickness also increasing to a larger extent. Though this rapid oxidation at high temperatures form the basis for the oxidative wear. You will have this high sliding speeds and that leads to very high frictional induced heat that leads to high temperatures of the contact. You will have a metal oxide thickness also increasing.

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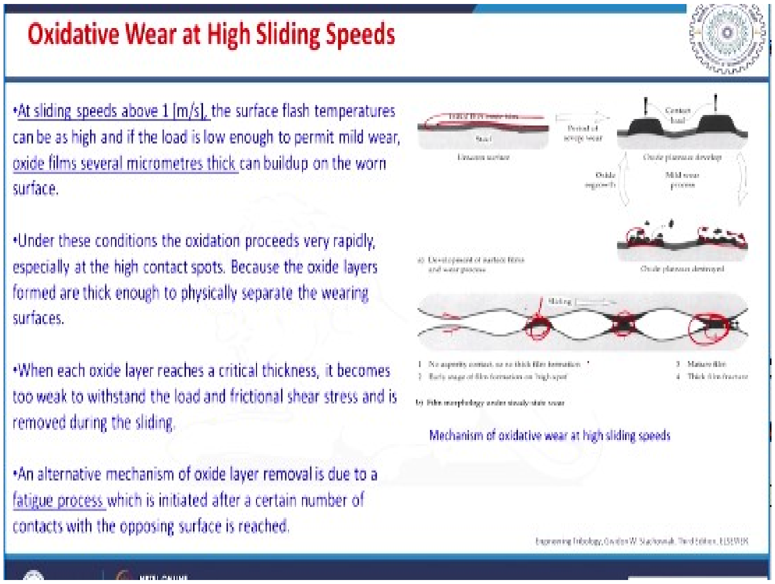

So, you will have a rapid oxidation at high temperatures form the basis of oxidative wear. With respect to sliding speeds, at sliding speeds above one meter per second generally, the surface flash temperatures can be high and if the load is low enough to permit the mild wear, oxide films of several micrometres thickness can build up on the worn surface. Under these conditions, oxidation proceeds very rapidly especially at high contacts spots.

Because these oxide layers formed are thick enough to physically separate the wearing surface, you will have a mild wear. So, initial thin oxide film and becomes contact loads and then the material is removed and again oxide is a re-grown again, it forms. When each oxide layer reaches a critical thickness, it becomes too weak to withstand the load and frictional shear stress, and layer is removed during the sliding.

You can see the no asperity contacts first of all and then asperity contacts leading to high hotspot, and then this material is removed. With increasing speeds, you have a difference in oxidative wear. An alternative mechanism can also be understood as the material is removed due to high fatigue process which is initiated after certain numbers of contacts with the opposing surface is reached.

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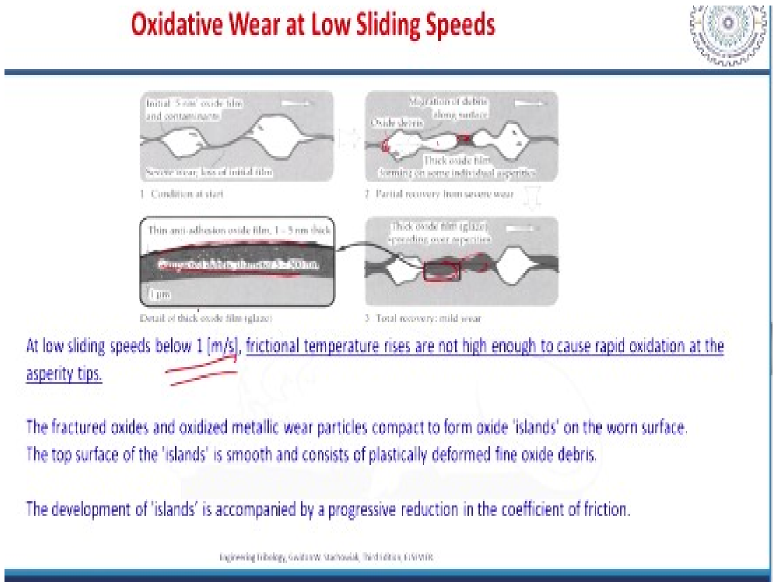

At low sliding speeds below one metres per second, the frictional temperature rises are not high enough to cause rapid oxidation at the asperity tips. So, the fractured oxides; you will see the oxide debris. Those oxidise compacts form oxide islands on the worn surface.

The top surface of this islands is smooth. These consist of plastically deformed fine oxide debris. So, development of such islands is accompanied by progressive reduction in the friction coefficient. You will have a compacted debris and then forming a layer which is plastically deformed. So, development of such islands is accompanied by the progressive reduction in the friction coefficient at low sliding speeds.

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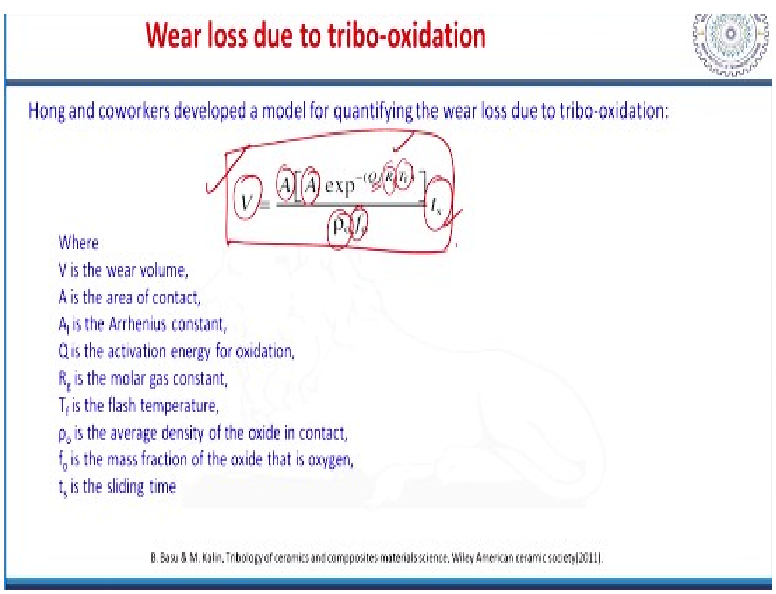

Finally, you can actually quantify the wear of the material due to tribo oxidation by this formula.

$$V = \frac{A[A_1 e^{-Q R_g T_f}]}{\rho_0 f_0} t_s$$

So, the wear loss due to tribooxidation; V is the wear volume, A is the area of contact, A_1 is generally Arrhenius constant and the activation energy required for the oxidation is Q, R is the molar gas constant, T_f is the flash temperature in absolute scale where ρ_0 represents the density of the oxide in contact and f_0 represents the mass fraction of the oxide that is oxygen.

So, f_0 is the mass fraction of the oxide, t_s is the total sliding speed. If you know that sliding time for a given material in the oxidative wear condition, you can actually estimate the material removal for this oxidative condition.

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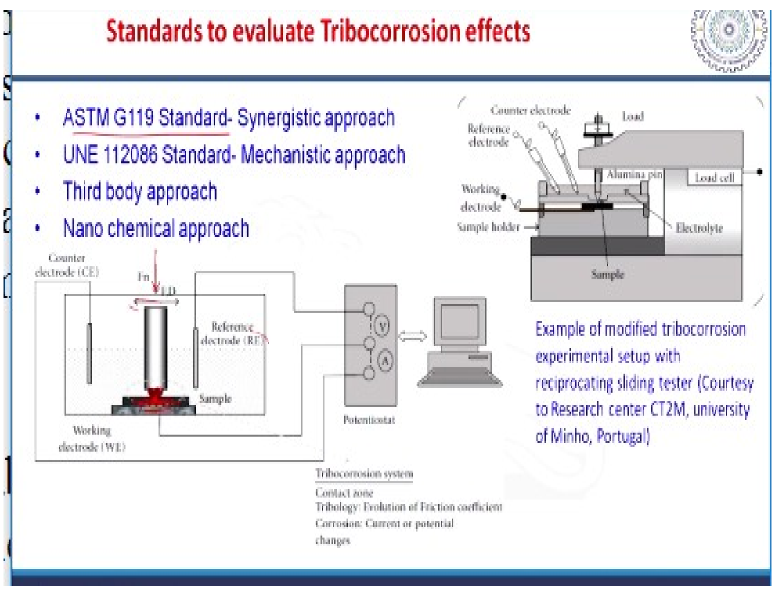

Finally, there are several standards available to evaluate such a tribochemical effects or we can say tribo corrosion effects. There is one ASTM G119 standard for the synergetic approach of this wear because of the mechanical contacts or wear because of the corrosion effects, both can be synergistically estimated. The wear by synergetic approach can be estimated by this standard. UNE 112086 standard for the mechanistic approach or third body approach or nano chemical approach.

There are several standards available to evaluate such tribochemical wear. So, these are all experimental approaches modified to evaluate the tribocorrosion wear. This is reciprocating when the load is applied. You can see is a reference electrode and a counter electrode. This is the specimen sample which is called working electrode. So, in a corrosive environment under loading conditions and reciprocating movement, you can actually evaluate the effect of this sliding in a corrosive environment.

The synergetic effects of this wear, mechanical wear and a corrosive wear that is tribocorrosion. There are certain standards available to evaluate the tribo corrosion effects.

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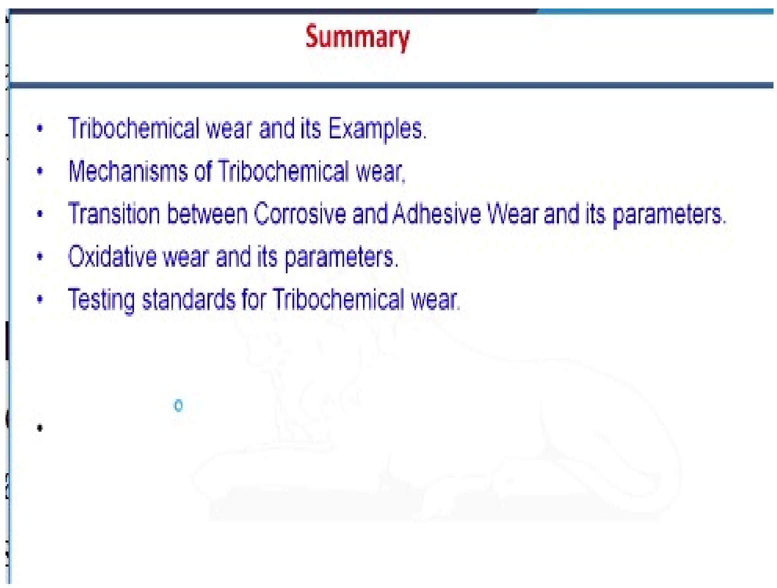

So, finally summarising this class, tribochemical wear and its examples are seen. Mechanisms of tribochemical wear are understood, and we understand there is a transition between the corrosive and adhesive wear and oxidative wear is also understood with their parameters. The wear loss due to tribooxidation can be estimated if you know the sliding speed, the temperature and other oxidative wear conditions for a given material.

And there are certain testing standards available for the evaluating the tribochemical wear. In coming case studies classes, we will see several examples of materials subjected to such a tribochemical wear conditions and then we will understand the mechanisms involved in the material removal under those conditions. So, for a given class of materials if the conditions of the wear are different, you will have a transition from abrasive or adhesive wear to tribochemical wear.

We will also see whether this tribochemical wear is beneficial in reducing the friction and wear or it is detrimental for wear and friction in coming classes, thank you.