**Friction and Wear of Materials: Principle and Case Studies**
**Prof. Bikramjit Basu**
**Department of Materials Research Center**
**Indian Institute of Science – Bangalore**

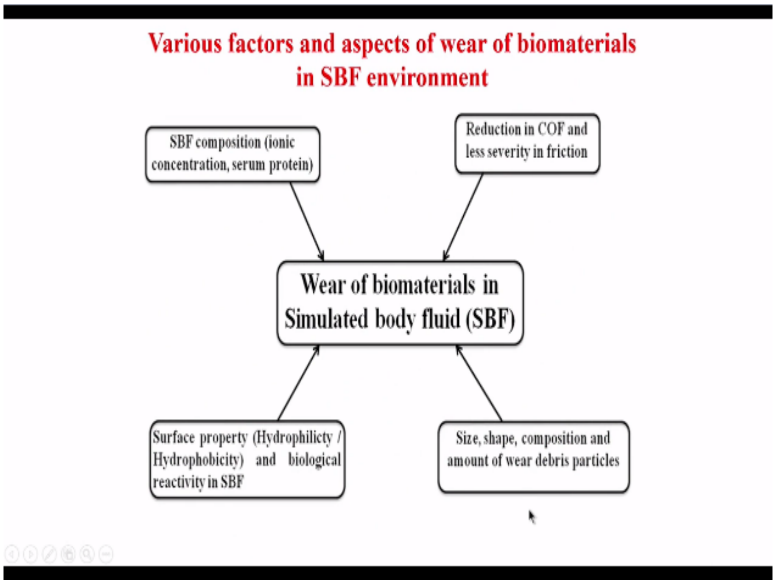
**Lecture - 22**
**Wear Behavior of Bioceramic and Biocomposites**

So welcome back to this NPTEL. Again, we will be continuing this Wear Behaviour of Bioceramic and Biocomposites. In the last lecture, I have given sufficient introduction, whatever of relevance to this particular NPTEL lecture in tribology, so here I will present another published case study from our own group and that is on the Glass Infiltrated Alumina.

**(Refer Slide Time: 00:58)**


So just to refresh your memory this that various physical and biological properties that need to be considered for an implant material like processing like what is the process ability to make complex shapes CAD-CAM designing to produce the desired shapes and porosity, Microstructure, like Microporosity and Macroporosity. Physical properties, lower density, Elastic modulus; in vitro Biomineralisation, Electrical Properties, in vitro biocompatibility, antimicrobial properties and in vitro biocompatibility.

**(Refer Slide Time: 01:24)**




So some of the things I think at certain point of time in previous lectures I have mentioned to some extent. Okay. Now, what are the different aspects of the biomaterials wear of biomaterials in simulated body fluid. Now these actually these slides summarizes four different factors. One is that SBF composition, ionic concentration and serum protein. Now in one of the earlier lecture I have mentioned that simulated body fluid contains different chloride salts and there some of the medal ions like sodium, potassium are important.

So this ionic concentration is important. Now in order to make the invariant more aggressive often people use 5 times or 10 times is wave concentration in terms of the SBF, 5x or 10x SBF is essentially where the ionic concentration has been increased to 5 times or 10 times and then serum protein. Second one, normally some of the earlier case study I have mentioned that it is possible to realize, reduce coefficient of friction and less severity in friction in case of the wear of materials in simulated body fluid.

Third one is surface property like hydrophilicity or hydrophobicity and how biological reactivity in SBF that changes that also influences the friction and wear. And forth one is very important, that is size, shape, composition and amount of wear debris particles. I think I have mentioned very categorically that this shape and composition of the debris particles as well as size they influence the inflammatory responses in the psychological body environment.

**(Refer Slide Time: 03:24)**

## WEAR OF GLASS-INFILTRATED ALUMINA

So one of the case study I must mention here in this particular lecture is a Glass-Infiltrated Alumina. So alumina, is one of the bioceramic materials but it is mostly bioinert materials because it does not have that much bioactivity like hydroxyapatite for example. But wear of Glass-Infiltrated Alumina it can be used for dental application for example.

**(Refer Slide Time: 03:53)**

## Chemical and Physical Properties of Supplied Substrate and Coating Substances

| Material | Composition | CTE ($X10^{-6}$)/$^0$C | Density (gm/cc) | Elastic Modulus (GPa) |
|---|---|---|---|---|
| Alumina (Substrate) | $Al_2O_3$ =99.5% and rest oxide impurities | 9.1 | 3.89 | 378 |
| Pyrex Glass (Coating Substance) | $SiO_2$ = 81% and rest oxide impurities | 3.2 | 2.23 | 62 |

So as the name suggest that you know, that you can use this normal glasses, Pyrex glasses which is used for coating, substances and you can have 99.5% purity alumina which is a coefficient thermal expression 9.1 to the -6 Kelvin inverse. And these are the standard numbers for elastic modulus density.

**(Refer Slide Time: 04:14)**

## Mechanical Properties of as-received Alumina (AS) and Glass Infiltrated Alumina (AG)

| Material | Ceramic designation | Flexural Strength (MPa) | Vickers hardness, $HV_5$ (GPa) | Indentation fracture toughness, $K_C$ (MPa. $m^{1/2}$) |
|---|---|---|---|---|
| Sintered Alumina | AS | $330 \pm 50$ | $17.6 \pm 1.6$ | $3.9 \pm 0.6$ |
| Glass Infiltrated Alumina | AG | $530 \pm 35$ | $19.2 \pm 1.2$ | $4.6 \pm 0.8$ |

Now when you use these two types of materials one is the Sintered Alumina and another one is the Glass Infiltrated Alumina. So AS is the AS-Sintered and AG is the Alumina Glass Infiltrated. So there is an increase in the flexural strength and this increase in flexural strength must be because of the compressive stresses that are generated on the glass infiltrated alumina because of the glass infiltration.

Vickers hardness increase to some extent from 18 to 19; 17.6 to 19.2. Indentation fracture toughness there is a very modest increase from 3.9 to 4.6. But if you look at the error bar I think it will be overlapping.

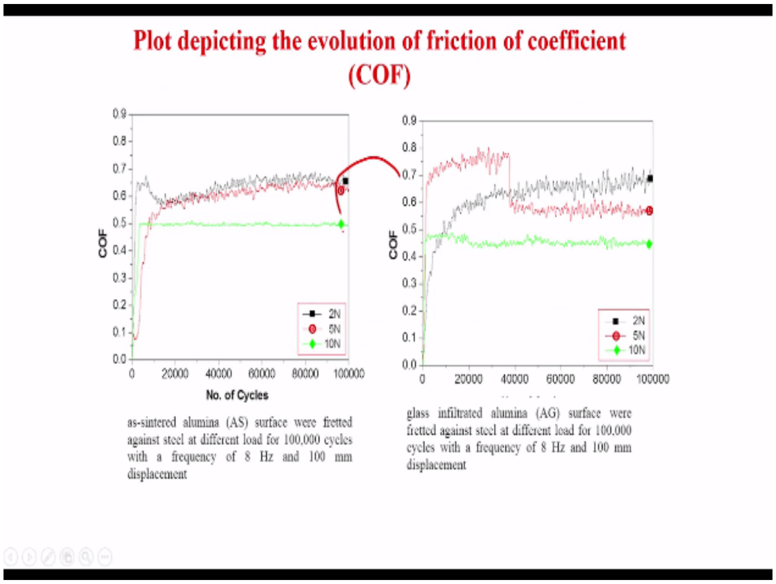
**(Refer Slide Time: 05:00)**

## Coefficient of Friction and Wear Rate of investigated materials, after being fretted at Various Load and Cycles

| Sample Code | Load (N) | No. of Cycles | Wear Rate $mm^3/Nm$ | COF |
|---|---|---|---|---|
| AG | 2 | 10000 | $1.5 \times 10^{-4}$ | 0.63 |
| | | 50000 | $6 \times 10^{-5}$ | 0.59 |
| | | 100000 | $7.5 \times 10^{-6}$ | 0.54 |
| | 5 | 10000 | $7 \times 10^{-5}$ | 0.57 |
| | | 50000 | $2.8 \times 10^{-5}$ | 0.54 |
| | | 100000 | $3 \times 10^{-6}$ | 0.52 |
| | 10 | 10000 | $5 \times 10^{-6}$ | 0.53 |
| | | 50000 | $2 \times 10^{-6}$ | 0.49 |
| | | 100000 | $1.5 \times 10^{-6}$ | 0.44 |
| AS | 2 | 10000 | $2 \times 10^{-4}$ | 0.62 |
| | | 50000 | $5 \times 10^{-5}$ | 0.58 |
| | | 100000 | $1.1 \times 10^{-5}$ | 0.59 |
| | 5 | 10000 | $9 \times 10^{-5}$ | 0.62 |
| | | 50000 | $3.2 \times 10^{-5}$ | 0.56 |
| | | 100000 | $5 \times 10^{-6}$ | 0.57 |
| | 10 | 10000 | $1 \times 10^{-5}$ | 0.56 |
| | | 50000 | $4 \times 10^{-6}$ | 0.52 |
| | | 100000 | $1.6 \times 10^{-6}$ | 0.49 |

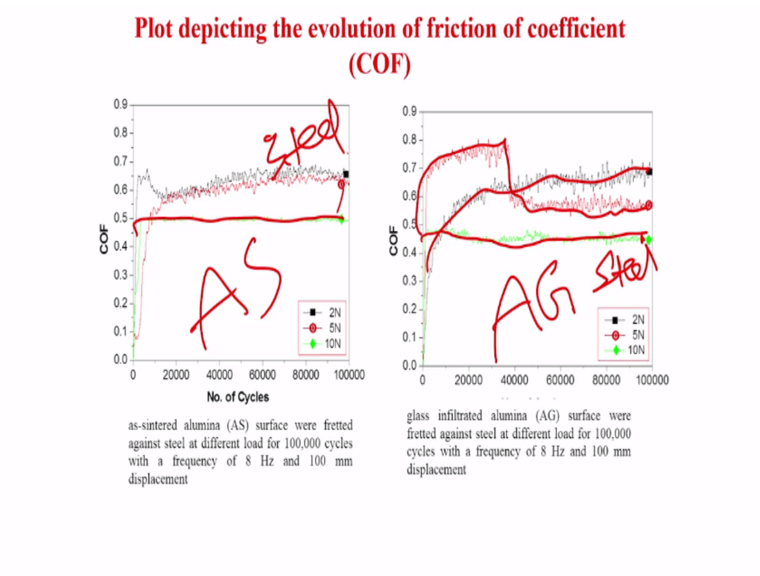
Now for any new materials we always test a different loading in the fretting wear tester in the different loading like we vary the load like 2 to 10 Newton in load for both Alumina Glass and Alumina Sintered Alumina and then what you do what we do we vary the number of cycles.

**(Refer Slide Time: 05:24)**




For example, if you look at this particular case that is the number of, so we can see that, that number of cycles is varies from 10,000 to 100,000 for alumina glass and alumina sintered. And then you can see that how wear it is changes. So it goes from 10 to the -4, 10 to the -6 so that means wear is reduced as you increase the number of cycles. And Coefficient of Friction it almost remains similar little bit decrease 0.63 to 0.54. The same thing you can see 0.56 to 0.49 like 0.56, 0.52, 0.49 that Coefficient of Friction is also reduced.

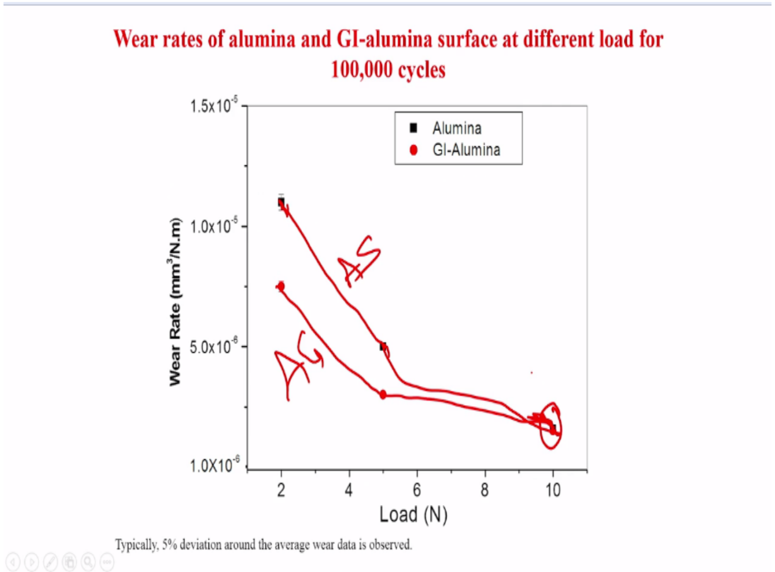
**(Refer Slide Time: 06:16)**




So this is one of the representative plots for the numbers coefficient of friction or friction evolution with number cycles. And this is for the AS that is the Alumina Sintered and this for AG that is the Glass Infiltrated Alumina. So what you clearly notice that higher the coefficient of friction, steady state is established relatively faster and it is maintained that is not much fluctuation.

These fluctuations normally we have observed at the lower load like 5 Newton as well as 2 Newton. But at 10 Newton load it is all stabilized and the coefficient of friction in both the cases Alumina Sintered and Glass infiltrated is 0.5 or less than 0.5. And this is the case for the steel as a counter body, okay. This is the case for the steel counter body material.

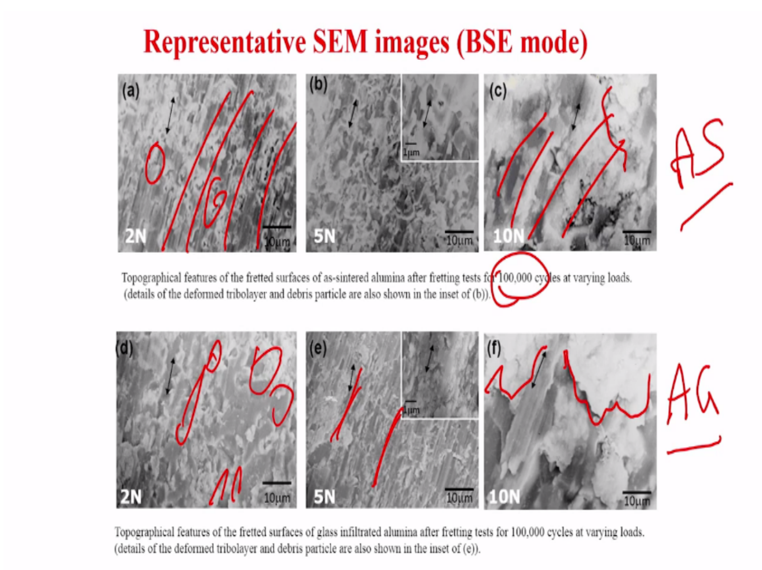
**(Refer Slide Time: 07:13)**




And that whatever data we have presented in the table and then you can see that how the plot is also when they are plotted against the load, so for Glass Infiltrated Alumina this where it is reduced but 10 Newton load is comparable, so when it is reduced with load but what you see what you observed in case of this as-sintered alumina the wear rate is also reduced but the wear rate between this two materials for both this, this is for the AS and this is for the AG.

For the AG material wear rate is lower at 2 Newton load and 5 Newton load, at a 10 Newton load they are more or less comparable.

**(Refer Slide Time: 08:05)**



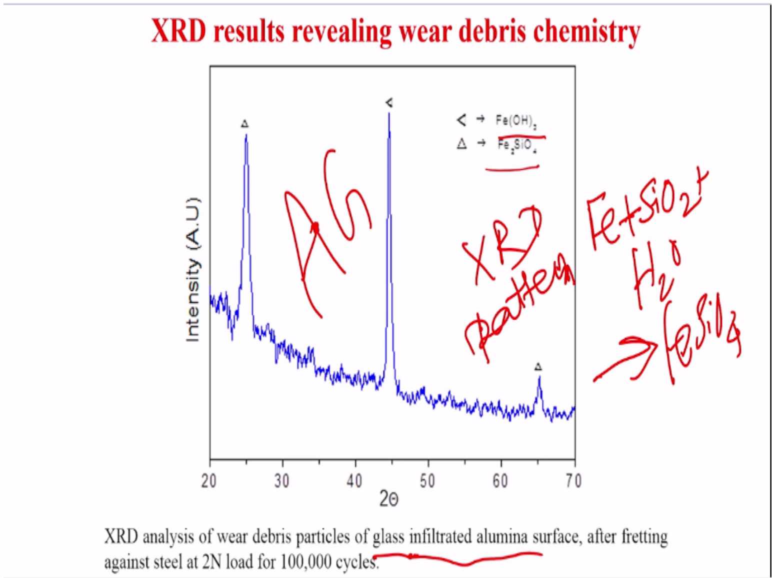
Okay. So this is the; so this is the bad scattered electron imaging which we have captured using scanning electron microscope of the own surfaces. Now if you look at the first row of the images what you see that first one is the 2 Newton then middle one is the 5 Newton and third one is the 10 Newton. So this is the topographical features on the AS-sintered Alumina after the fretting test 100,000 cycles that is the, at the end of the 100,000 cycles we have taken this images.

What you notice that there is clearly a signature of this tribochemical layer formation and also this abrasive scratches which is somehow is reduced because of the extensive tribochemical layer formation. And there is some observations of cracking also at the 10 Newton load. Now if you look at this Glass Infiltrated Alumina this is the AG and this is for the AS.

If you look at the Glass Infiltrated Alumina at even in the 2 Newton load which is very small, small load there itself you can see very bright contrast area, this is the tribochemical layer and 5 Newton load this tribochemical layer formation is clearly visible but much less. But at 10 Newton load you can see very thick dense tribochemical layer formation which really appears in a different contrast.

What it means is that this tribochemical layer has a different chemistry compare to that of the unknown surfaces that is why they appear in a different contrast. Other things, if you compare this AS versus AG again the contrast of the tribochemical layer is qualitatively similar. What it means, like an AS in case of AG also tribochemical layer with different chemistry that forms.

**(Refer Slide Time: 10:09)**



XRD analysis of wear debris particles of glass infiltrated alumina surface, after fretting against steel at 2N load for 100,000 cycles.

Now therefore, it is important to know, what is this tribochemical layer or what is this wear debris chemistry? We have conducted the XRD, so this the XRD patterns where intensity is plotted again the 2 theta, and what you notice here that there are phases which are formed this is Fe2 SiO4 and Fe2 OH2, so these are the phases which are forms as a result of the tribochemical reactions.

So you have a steel in the counter body and steel is also reacts with SiO2 and + in the humidity you can put is that H2O. So then it can form is that Fe SiO4. Okay. So now these are the kind of potential reactions that can takes place and steel also can be; this hydroxide; r1 is also can also be formed because this materials are fretted against the glass steel counter body.

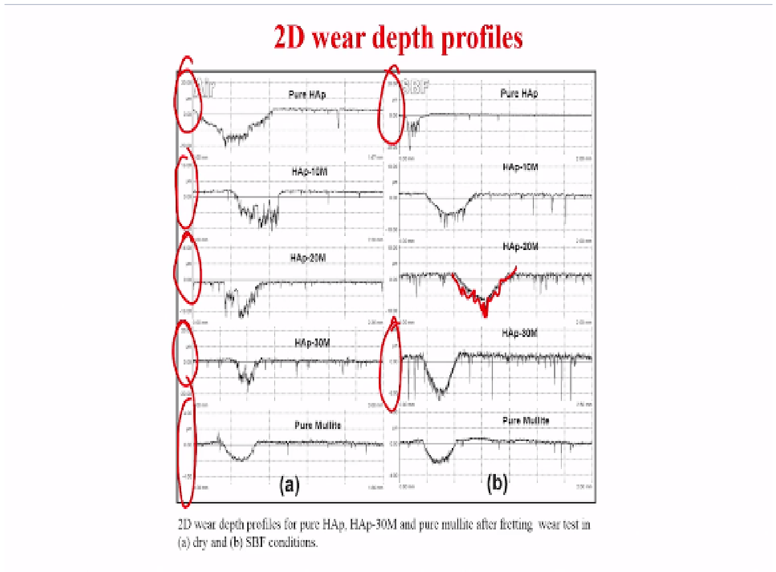
And this is the case for the AG not AS that were is the glass infiltrated alumina. But the extra peaks are quite sharp essentially showing that this phase which is formed at this particular after the friction fretting wear of this materials they are essentially crystalline phases. So this crystalline iron, silicate or Fe2 SiO4 hydroxide both are forms after the fretting at 2 Newton load.

**(Refer Slide Time: 11:54)**


So let us now switch to another materials systems where we have done also some study and that is Hydroxyapatite Mullite Composites. So why hydroxyapatite mullite composites? Because hydroxyapatite is a bioactive material but hydroxyapatite does not have good physical properties in terms of the hardness and strength.

Mullite is the solid solution of alumina and silica. So essentially Mullite has a typical composition of 3:2, 3 Alumina and 2 Silica, so it is a solid solution of alumina and silica in 3:2 ratio, and when you add Mullite to hydroxyapatite we are expecting that there increase in the hardness and strength of the material. This announcement of the hardness and strength is equally important because for the tribological applications if a wear is dominated by abrasive wear, then the increase in the hardness can meet to greater wear resistance of the materials.

**(Refer Slide Time: 13:11)**

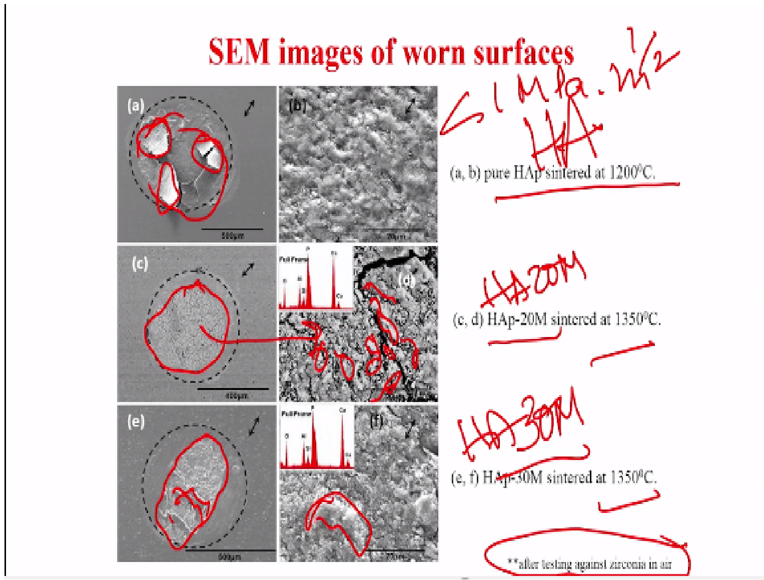



Now again we have done the different, we have used the different flat materials or where we have varied the mullite content, like 10% mullite, 20% mullite and 30% mullite. For reference, we have used both the hydroxyapatite as well as the mullite flat samples. Now what you notice that after the fretting work at the simulated body fluid in the simulated body fluid this the 2D surface depth profile of the region which experiences maximum wear.

The top one is the hydroxyapatite without any mullite. Next one from the top is the hydroxyapatite 10% mullite then 20M is 20% mullite, 30M is 30% mullite and then last one is the Pure Mullite. So the left panel is essentially for ambient environment; right panel is for simulated body fluid environment. Now the scale for all these along the y-axis which indicates the depth of this profile after using different kind of materials that scale is quite different. So for example, if you look at the first one it is essentially 20 micron is the scale.

The second it is for 10; this is again for 20 micron and this lower one is the 4M. So Mullite as expected Mullite is because Mullite is much harder so even for this third one is also for 6M, second from the bottom here again the scale is 6 micron. So while qualitatively you can see that there is wear square and there is lot of hills and valleys in this particular wear profile but quantitatively the wear depth is certainly different. And this wear depth the difference in the wear depth can be ascribe to that difference in the hardness of the material.

**(Refer Slide Time: 15:31)**



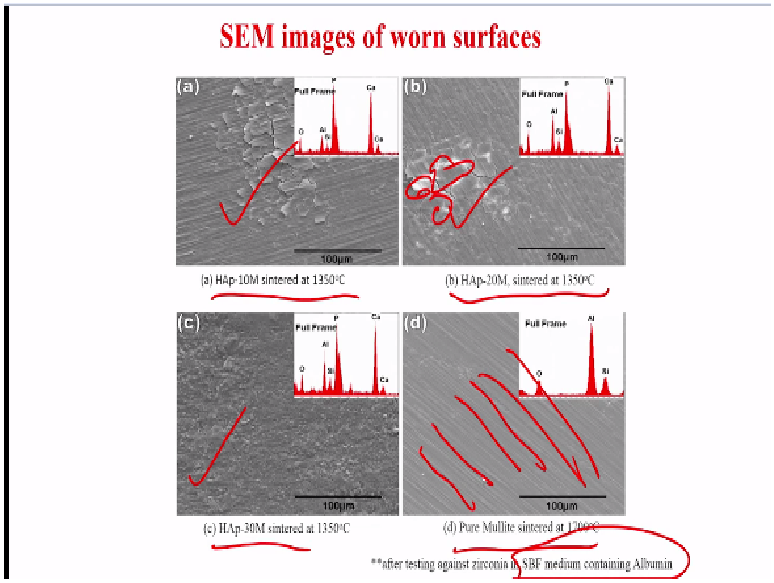

As I said before that wear mechanisms study is of central importance in the; for material scientist who work in the area of tribology. So we always do this; can you let me microscopy investigation or transmission of microscopy based analysis of the wear debris or own surfaces wherever it is possible. Now if you see the first panel the top one is for hydroxyapatite which sintered at 1200 degree Celsius after the wear is over; after testing against zirconia in; after zirconia in conditions.

The second one is HA20M that is 20 mullite. Third one is HA30 mullite, that is after sintered at different temperature like one is 1200, the second and third one 1350 degree Celsius. What you see in the hydroxyapatite case, you see there is a regions of exfoliation and this exfoliation is very typical of some of the brittle materials because hydroxyapatite as a flexural toughness of less than 1 MPA square root meter.

So it is much, much brittle then that of the alumina because alumina flexural toughness is around 3 or little higher than 3MPA square root meter so hydroxyapatite is extremely brittle. Second observation is that, after testing with hydroxyapatite 20% to alumina you can see that large region of the own surface is fully covered with the tribochemical oxide layer.

And this if you look at this particular region little bit closely you see that there are wear debris particles which are being interrupt on this particular own surface. Now the formation of the tribochemical layer is also equally observed after testing in hydroxide 30% alumina and their you can see the signs of delamination but here there is a very dense tribological layer and wear debris that is formed under own surfaces.

**(Refer Slide Time: 17:47)**

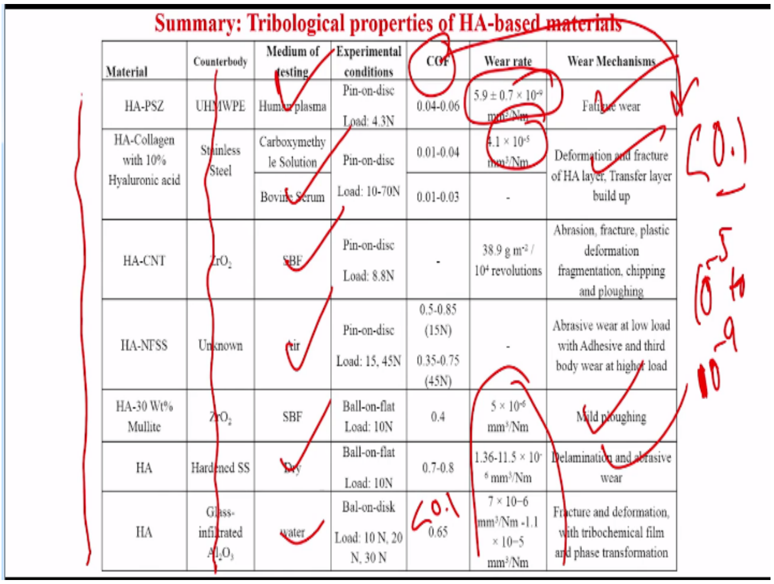



Now this; this is; so the last one you seeing the Ambient environment okay. Now, one would be very interested to see, how does this wear mechanism change in the simulated body fluid medium containing the Albumin. And simulated body fluid medium you can see that have 20% alumina, have 10% alumina, have 30% alumina, your mullite. And what you notice that here also there is signs of delamination cracking and tribochemical layter. In Pure Mullite, it is simply that abrasive wear. Okay.

So whatever you see 10% mullite, 20% mullite, 30% mullite that this changes in the wear mechanisms must be attributed to the presence of other phases rather than mullite, simply because mullite when they are fretted against zirconia in simulated body fluid they only show abrasive scratches. So the presence of mullite in the composites can be attributed only to the generation of abrasive scratches.

What our additional observation one can notice from this particular SEM, this particular, this particular SEM image must be due to the presence of any reaction phase which is formed because of the interaction within hydroxyapatite and mullite at the sintered temperature that would additional influence to the formation of the tribochemical layer.

**(Refer Slide Time: 19:25)**



**Summary: Tribological properties of HA-based materials**

| Material | Counterbody | Medium of testing | Experimental conditions | COF | Wear rate | Wear Mechanisms |
|---|---|---|---|---|---|---|
| HA-PSZ | UHMWPE | Human plasma | Pin-on-disc Load: 4.3N | 0.04-0.06 | $5.9 \pm 0.7 \times 10^{-9}$ $mm^3/Nm$ | Fatigue wear |
| HA-Collagen with 10% Hyaluronic acid | Stainless Steel | Carboxymethyle Solution | Pin-on-disc Load: 10-70N | 0.01-0.04 | $4.1 \times 10^{-5}$ $mm^3/Nm$ | Deformation and fracture of HA layer, Transfer layer build up |
| | | Bovine Serum | | 0.01-0.03 | - | |
| HA-CNT | $ZrO_2$ | SBF | Pin-on-disc Load: 8.8N | - | 38.9 g $m^{-2}$ / $10^4$ revolutions | Abrasion, fracture, plastic deformation fragmentation, chipping and ploughing |
| HA-NFSS | Unknown | Air | Pin-on-disc Load: 15, 45N | 0.5-0.85 (15N) 0.35-0.75 (45N) | - | Abrasive wear at low load with Adhesive and third body wear at higher load |
| HA-30 Wt% Mullite | $ZrO_2$ | SBF | Ball-on-flat Load: 10N | 0.4 | $5 \times 10^{-6}$ $mm^3/Nm$ | Mild ploughing |
| HA | Hardened SS | Dry | Ball-on-flat Load: 10N | 0.7-0.8 | $1.36\text{-}11.5 \times 10^{-6}$ $mm^3/Nm$ | Delamination and abrasive wear |
| HA | Glass-infiltrated $Al_2O_3$ | water | Bal-on-disk Load: 10 N, 20 N, 30 N | 0.65 | $7 \times 10{-}6$ $mm^3/Nm$ -1.1 $\times 10{-}5$ $mm^3/Nm$ | Fracture and deformation, with tribochemical film and phase transformation |

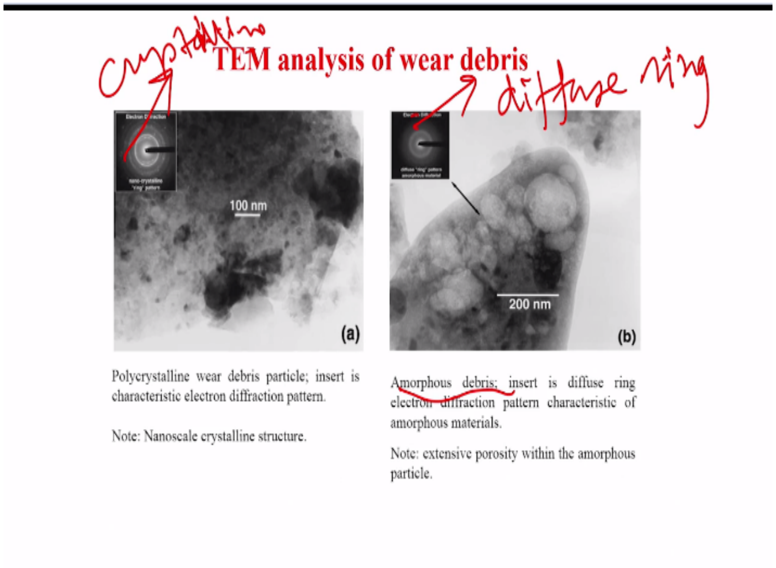


Now this is how the, that what we have published little 4 or 5 years ago that what is the Tribological properties the summary of hydroxyapatite based materials. What you notice here that along this left most column your hydroxyapatite based materials are there. What is the counter body? UHMWPE, polyethylene, then Zirconia then Glass Infiltrated Alumina.

What are the medium of testing? Either plasma or Bovine Serum of Ambient Environment or SBF or Water. Now if you look at the coefficient of friction most of the cases the coefficient of friction in this cases is 0.1. The Coefficient of Friction is less than 0.1. Wear rate, it can wear it 10 to the -5 to 10 to the power -9.

So depending on what is the material, what is the simulated body fluid composition you can get wear rate values between 10 to the -5 to 10 to the -9 millimeter cube/ Newton meter. Wear mechanism it is Fatigue wear, Deformation and fracture, Mild ploughing and Delamination and abrasive wear. So this is the total summary of what we have observed for the tribological properties of this hydroxyapatite based materials.

**(Refer Slide Time: 20:50)**




Now there also evidence this of that phase transformation of this zirconia particularly after the fretting wear often tetragonal zirconia transforms to orthogonal zirconia and so on before they go to transformation to monolithic zirconia. So this is the bright field transmission electron microscopy images of the Polycrystalline wear debris particles where you can see the insert is the characteristic electron diffraction pattern and you can see the Nanoscale crystalline structure.

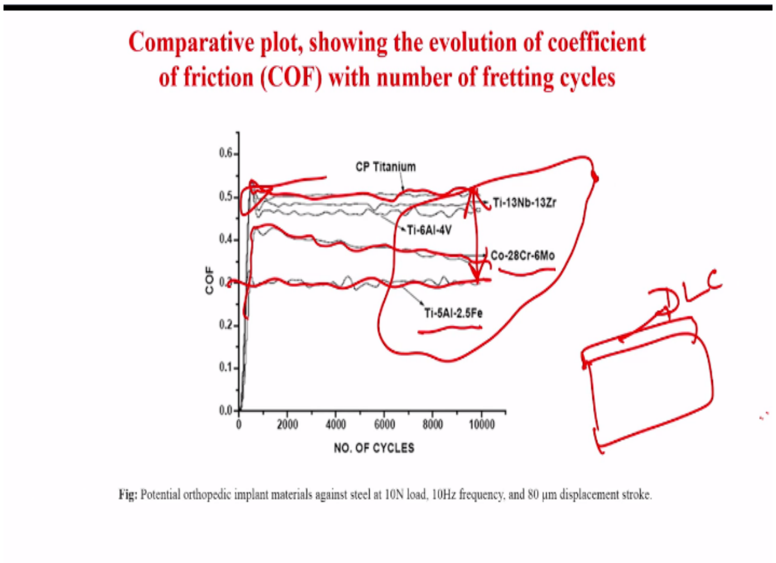
But here this is the some other work by Michelle Kalin where you can see very Amorphous debris formation. So Amorphous debris formation, it is clear from the diffused ring, so if you selected a different pattern, if it is a diffused ring then it is amorphous debris formation and this is for the crystalline page because this is a spot pattern in the selected here diffraction pattern. So TEM analysis actually is very useful.

Because in the transmission electron microscope images you can get selected area diffraction pattern from the very localized region. And if you look at the other contemporary measurements for example, scanning electron microscopy or X-Ray diffraction, X-Ray diffraction to some extent is possible, Raman spectroscopy and so on. It is very difficult to conform with greater assurance that this debris particles are indeed crystalline or amorphous.

But TEM actually gives you very clear idea about the nature of the debris particles. Now if the debris particles are crystalline which is the case of the three body wear situation and then they can contribute to the further where depending on the hardness difference between the debris particles and one of the matting solids then it will cause wear of the software of the matting solids.

The same thing is true for the debris particles in case of the amorphous but amorphous materials because they do not have the crystallinity so in the amorphous case it is quite unlikely that they will cause lot of wear. However, under stress of the friction and surfaces often amorphous were debris particles can undergo crystallinity.

**(Refer Slide Time: 23:22)**




So before I finish this particular lecture on the Wear behavior of bioceramic and biocomposites, it is not only the bulk materials but also researchers use various surface coatings. For example, you can have titanium materials but you can put this surface coating on the titanium for example DLC Diamond-Like Carbon Coating. But this is the case for the friction in wear properties of some of the titanium based materials without any coatings.

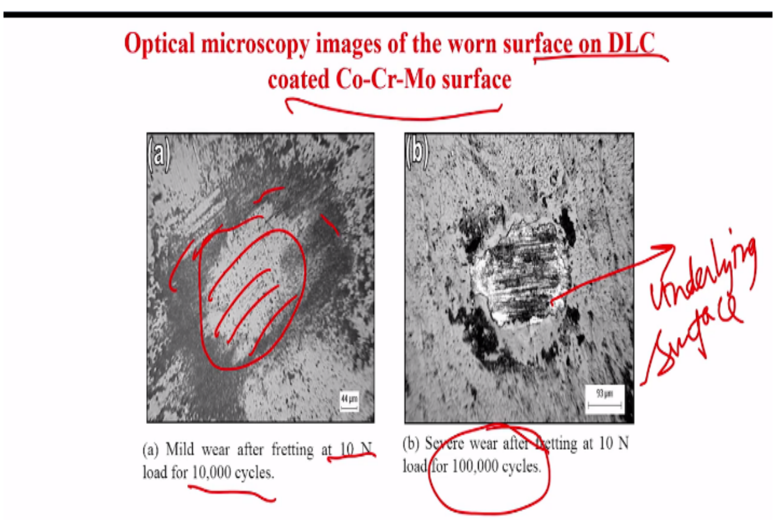
And here you can see that there is a serious of titanium based alloys which are of relevance to clinical applications. For example, titanium 13% erbium, 13 zirconia, Ti-6Al-4V which extremely widely used or Titanium 5% aluminum 2.5% iron. Now this titanium alloys actually is an area which is very extensively pursed by the metallurgist and metallurgist they use different allied in an approaches to bring in some of the outstanding properties in the titanium based alloys.

And these 3 alloys has adjust some examples, three examples from this very large pool of the titanium based alloys. And when you see that; when that there friction properties are compared with the commercially pure titanium depending on the alloying elements addition or depending on the alloy composition it is possible to get a realize a much reduced coefficient of friction.

For example, if you compare with a titanium 5% of aluminum 2.5% add-on one can get confuse in 0.3 and this is the 0.3 but when at the commercially pure titanium it is around 0.5. So there is clear and distinct advantages of using the titanium based alloys in biomedical applications because one can bring down the coefficient of friction from 0.5 to 0.3.

When compare to the titanium based alloys, another materials which is use for orthopedic application is a cobalt chrome. So cobalt 28% chromium, 6% mullite alloys and this is use for the knee-replacement applications and this knee-replacement applications if you see that again their coefficient of friction is fairly close to 2.3 to 2.4 or it is less than 0.4 against steel as a counter body materials.

**(Refer Slide Time: 26:07)**



As I said before that one can use that Diamond-Like Carbon Coating or Titanium Nitride Coating and so on orthopedic bearing surfaces to reduce coefficient of frication in wear. So this is just an example that these Diamond-Like Carbon Coated, Cobalt chromium allie alloys after coating without coating and with coating.

So this is that Ontialci coated cobalt chrome allie cobalt chrom allie, so this is at 10 Newton load, 10,000 cycles. This is the coated surfaces. This is not uncoated surfaces. You see that there is signs of this debris particle but there is some scratches. But you do not see any underlying surface. But at 10,000 cycle what you see this is quite contrast, this is like underlying surface.

What it means that this coating can survive only < 100,000 cycles. After 100,000 cycles you can clearly see that coating gets piled up or coating is abraded away, exposing the underlying surfaces to wear, which is not desirable. So this kind of fretting wear experiments essentially are very useful to also quantitatively, evaluate the durability of this coatings under tribological conditions.

Now this is also, this is also another thing that one can understand that it is not only understanding the friction wear mechanisms for tribological surfaces but also it is important to know what is the stability of this coatings under the tribological conditions in terms of the time scales, so that if the coating is done then their underlying materials can lead to much more severe wear. So with this examples, I think I end this particular lecture and I will come back to the next lecture in this NPTEL series. Thank you.