

**Friction and Wear of Materials: Principles and Case Studies**  
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**Lecture – 24**  
**Wear of Transformation Toughened Zirconia**

So in last few lectures, I have emphasized need for biomaterials development, particularly bioceramics and composites. And I have also discussed that how the elastic modulus properties of high density polyethylene materials can be tailored and tuned to obtain desired wear resistance properties.

And if you remember that high density polyethylene hydroxide with alumina based hybrid composites, they are quite, they are being developed for orthopaedic applications, particularly as a potential alternative to acetabular socket for total hip joint replacement. So in today's lecture, what I am going to do is that I am going to discuss that friction and wear properties of transformation toughened zirconia.

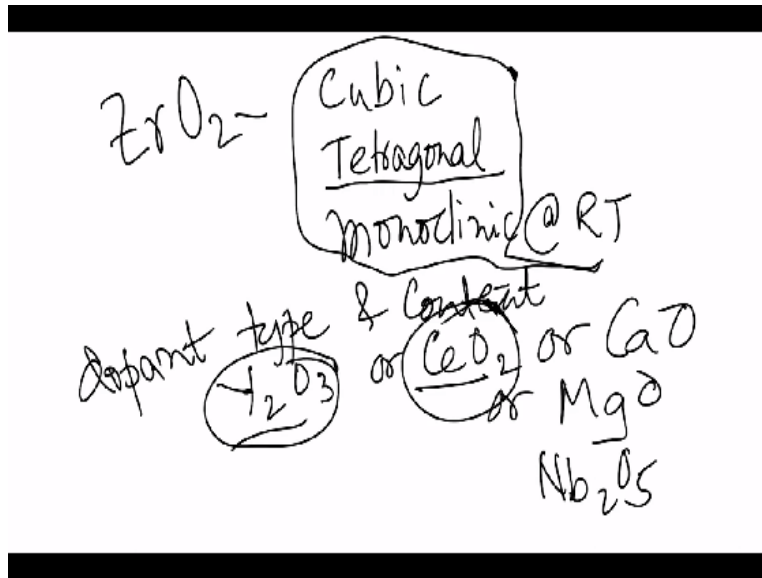
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**Wear of Transformation Toughened zirconia**

So in case of friction and wear of the transformation toughened zirconia, it is very important to realize that how one can tailor fracture toughness of this zirconia based ceramics.

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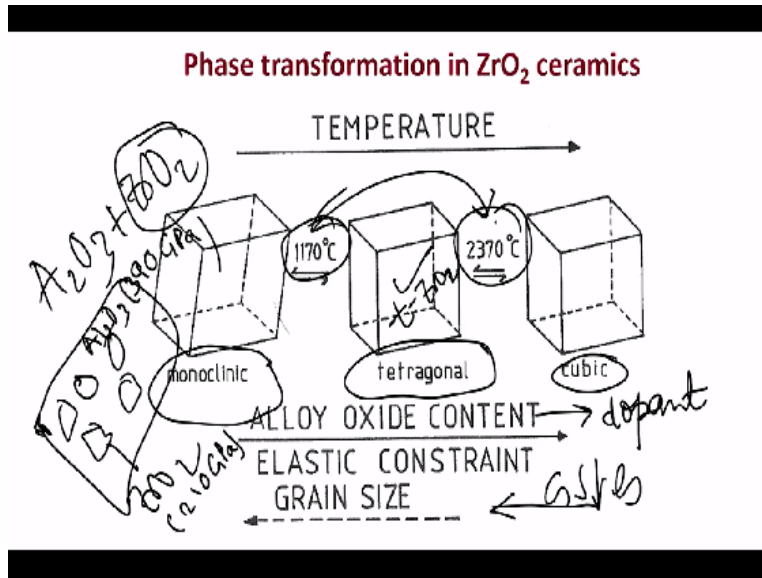


Now those who are not from ceramic background, it is important to understand first that what is transformation toughening in zirconia ceramics. First of all, zirconia, they have 3 polymorphs. So you have a high temperature phase that is cubic phase. Then comes tetragonal phase in the intermediate temperature region. And then comes monoclinic phase. Now at room temperature, it is the monoclinic phase.

Now depending on the dopant content, what is dopant? For example, depending on the dopant type and content. Now what are the dopant types? Dopant type can be either yttria or ceria or calcium oxide or magnesium oxide. These are the different oxide dopants which can be, even niobium oxide also, niobium doped zirconia is also possible. These different type of oxides can be doped to zirconia and these will have an influence on the phase stability of zirconia.

So phase stability of zirconia in a sense that although the tetragonal phase is not thermodynamically not stable at room temperature but we in yttria doped zirconia, tetragonal phase can be retained at room temperature. So there is a compositional effect and because of this compositional effect, the thermodynamic property of the system also changes and that allows the tetragonal phase to be retained at room temperature. So this is one of important things that one should remember.

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Now as far as the typical phase transformation temperature is concerned, cubic phase is stable above 2370 degrees Celsius. Between 1170 and 2370, it is the tetragonal phase which is stable and below 1170 degrees Celsius up to room temperature, it is the monoclinic phase which is stable. So these are the 3 major polymorphs of zirconia. Now as I said, this alloy oxide content is nothing but dopant content.

So dopant content I have just mentioned. So if your dopant content increases, what it means that this particular tetragonal phase, what we call is t-zirconia phase, is stable at room temperature, okay. And if your elastic constraint in the matrix also increases, for example, if you add zirconia to alumina matrix. So you have that pure alumina and then you add little bit of zirconia in the alumina matrix.

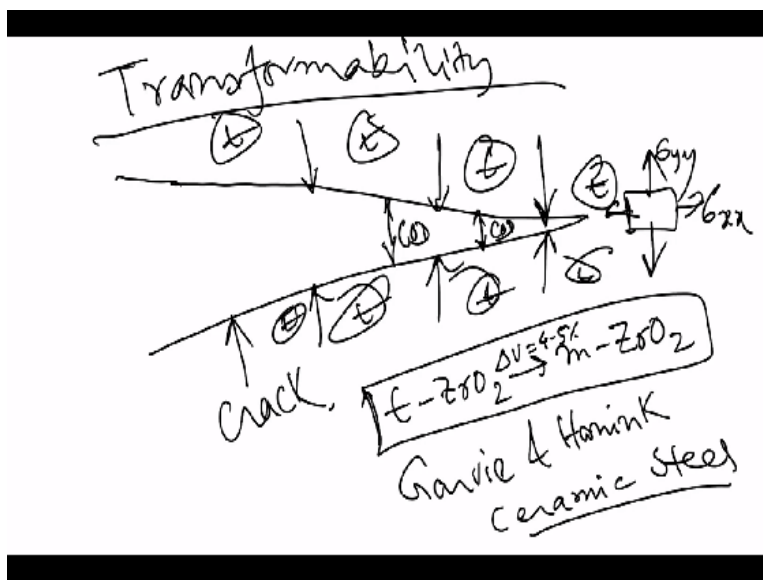
So zirconia, these are the particles, right. These are the zirconia particles. But if these zirconia particles is constrained in an alumina matrix. Now alumina, their elastic modulus is 390 gigapascal. Whereas zirconia, their elastic modulus is 210 gigapascal. Now by dispersing zirconia in alumina matrix, essentially you are allowing the zirconia particles to experience larger elastic constant in their neighbourhood.

Because all the alumina grains or the alumina grains which are part of the alumina matrix, they have higher elastic modulus. And accordingly these, because of the elastic constraint, the

zirconia, that higher to high temperature tetragonal phase can be retained. So essentially it will not allow tetragonal phase to undergo phase transformation to monoclinic phase. So I repeat there are 3 effects that which will influence or which influences the zirconia phase stability.

The first one is the dopant content. Second one is the elastic constraint. And third one is the grain size. Grain size means if the grain sizes increases, then what happens? The tetragonal phase can transform to monoclinic phase. But if the grain sizes decreases, that means if the GS decreases, then what will happen? Even the tetragonal phase also can be retained down to room temperature. Now why there are so much enthusiasm about these zirconia phase stability?

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Because a couple of decades ago, these group of Australian researchers like R. C. Garvie, Richard Hannink, they wrote a paper in nature and this paper title was ceramic steel. And that causes lot of enthusiasm in the community. In a simplistic manner, let me explain that why tetragonal phase? Suppose this is a crack t, suppose this is a crack. So around the crack phase, if tetragonal phase zirconia is retained in the phase and then a crack tip has a particular stress field, right, in the tensile stress field.

Now in the crack tip stress field, suppose this is sigma xx, this is sigma yy and (()) (07:23), suppose in the crack tip stress field, this is your t phase, tetragonal zirconia phase. If tetragonal zirconia phase, they transform to monoclinic zirconia, I am just trying to explain you tetragonal

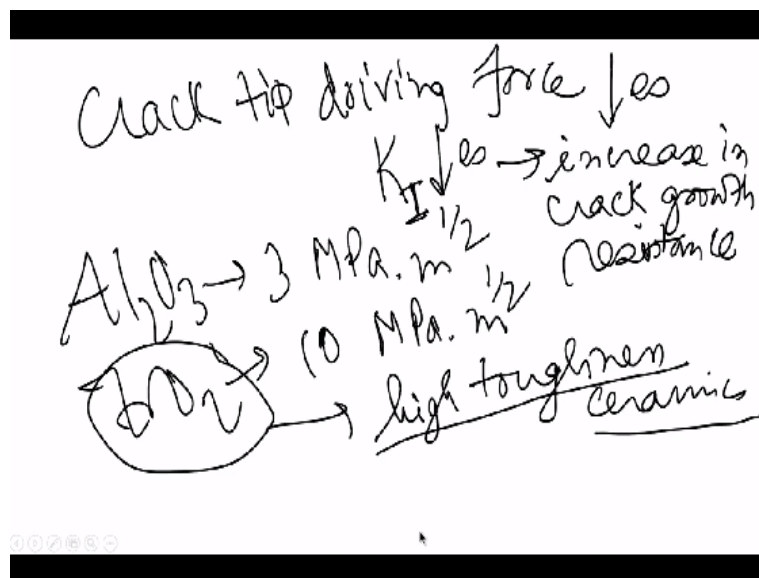
zirconia has always a desire to transform to monoclinic zirconia phase. Now if tetragonal zirconia transforms to monoclinic zirconia, typically there is a volume expansion of 4% to 5%.

So 4% to 5% volume expansion, what it does? It will induce the compressive stress on the crack tip. And if these compressive stresses are realized at the crack tip, then what will happen? This crack opening displacement, that COD, this is called COD that is called cracked opening displacement.

So this crack opening displacement is reduced and therefore, the crack tip will be blunted. So from this very basic information or very basic information that how tetragonal zirconia can influence the crack growth resistance in the microstructure. It should be clear to the students that this tetragonal to monoclinic zirconia can be invoked at the crack tip.

And that will lead to the crack tip closure or crack tip blunting that will lead to the increase in the crack growth resistance, ultimately K<sub>1C</sub> that mode I critical crack, tip fracture toughness also would increase. So if the driving force for the crack propagation is reduces, that leads to the increase in the fracture toughness. So the couple of things that let me also tell you in another slide.

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So this other things that I wanted to discuss that if the crack tip driving force for crack

propagation or driving force available at the crack tip if that decreases, if that decreases that means stress intensity factor at the crack tip decreases. So if stress intensity factor decreases, that will increase to that KI that is, so if this KI decreases and that leads to increase in the fracture toughness or increase in crack growth resistance, okay.

So for example, alumina, their fracture toughness is around 3 MPa square root meter. For zirconia, their fracture toughness is around 10 MPa.m square. So that is why zirconia is one of the materials which is considered as the high toughness ceramic, okay. So toughness is one of the important things, that toughness is essentially a measure of the crack growth resistance. So typically ceramics are known for the inherent brittleness.

And fracture toughness if that is increased, then the application of the ceramics also would widen. So therefore, there is a general trend in the ceramic community to understand and utilize the transformation toughening of zirconia in various other ceramic systems. But in this particular case study, what I am going to follow is that how to tailor the fracture toughness of the ceramics so that it leads to better wear resistance properties.

The question that I am going to address that does it mean that if you develop ceramics with better toughness properties, does it mean that it will always lead to better wear resistance properties or in other words is the toughness for transformation toughened ceramics is important and therefore, toughness of the transformation toughened ceramics should be carefully tailored in order to develop materials with tailor wear resistance property.

These may not be the case for non-transformation toughened ceramics like alumina or silicon carbide and those kind of non-transformation toughened ceramics. But for zirconia, it is fairly important as you will see in next 15 minutes or so that our results have shown a few years back that it is indeed important to tailor the fracture toughness in order to optimize the wear resistance property.

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**Wear of ceramics**

Wear of materials is a system property!

► Factors influencing wear of ceramics

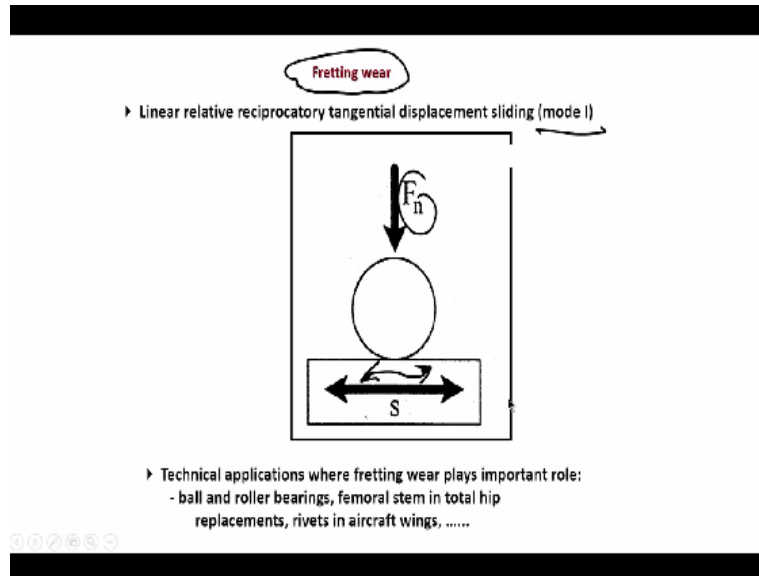
- Friction couple (flat/ball combination)
- Contact condition (dry/lubricated)
- Contact configuration (pin-on-disk, ball-on-flat etc.)
- Surface roughness of contacting surfaces
- Microstructure (grain size, phase assemblage, ..)
- Mechanical properties (hardness, **toughness**)
- Experimental parameters (load, duration, frequency, displacement)

Now let us go back to the slides again. So we have seen this particular statement at various time points in this NPTEL lecture and I would like to re-iterate again that wear of materials is a system dependent property, is a system property. So I repeat wear rate of stainless steel does not mean much unless one would specify that wear of stainless steel against alumina or wear of stainless steel against zirconia.

Now what are the factors that would influence the wear of ceramics? One is the friction couple like flat and ball combination. Second one is the contact condition, that dry or lubricated contact conditions. Third one is the contact configuration like pin-on-disk, ball-on-flat, etc. Fourth one is the surface roughness of contacting surfaces.

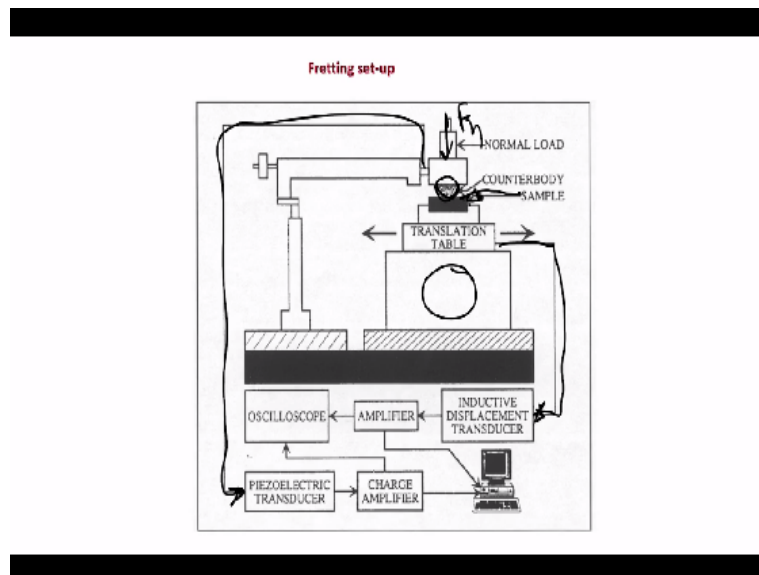
Microstructure grain size, phase assemblage, etc. Mechanical properties, hardness and toughness. I have put toughness with a different color for just to emphasize that in this particular case study, I will show how toughness also plays an important role in determining the wear resistance of this ceramics. And last one is the experimental parameters like load, duration, frequency, displacement, etc., okay.

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So like in some of the earlier case studies, we also used that fretting wear of this transformation toughened zirconia ceramics and this is the fretting wear of the mode I that is linear relative reciprocatory tangential displacement sliding. So you apply the load. Again this is a typical ball and flat type of configuration where the flat is given a linear reciprocatory sliding of very small amplitude like 80 micron and so on. And these fretting wear has major applications like in ball and roller bearings, femoral stem in total hip joint replacements and so on and so forth.

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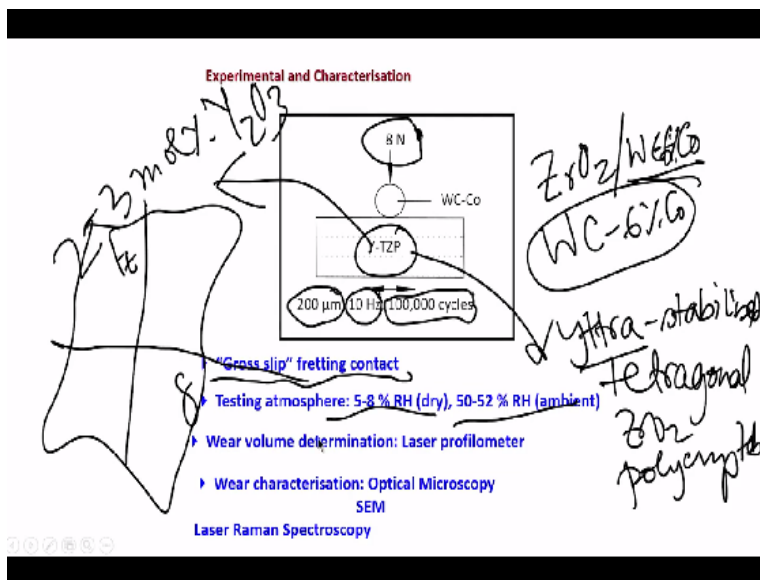


So this is the setup, the fretting setup that we have used in our experiments and this is the normal load that we are adding like a fan and this is the ball, this is the ball that we use. We can use zirconia ball, we can use alumina and so on. but in this particular case study, we have used

zirconia balls. And this is your translation table and this is your sample. So you have an inductive displacement transducer.

So where your, while you induce, while there is a stator motor which will give this motion. But also you can quite well control this displacement. And also you have a piezoelectric transducer just to record your frictional forces and there is a charge amplifier, oscilloscope and so on, so which help us to record this one.

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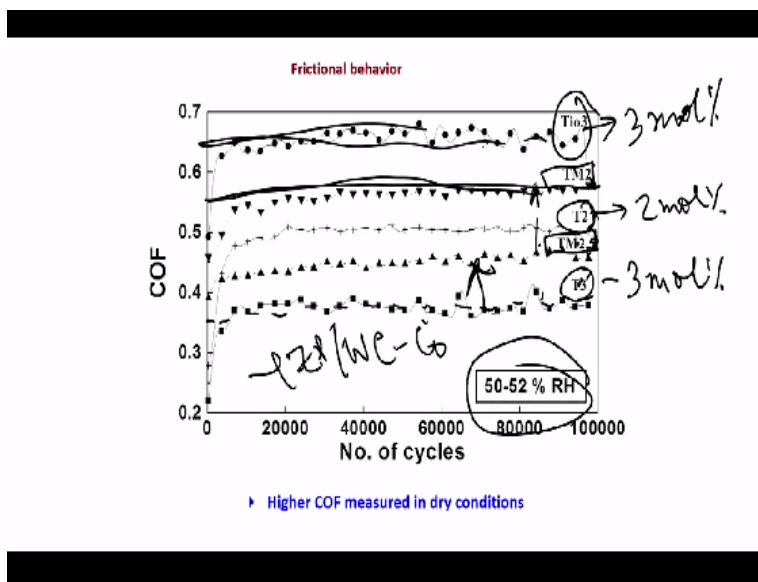
So we have not only used zirconia in one of our studies again transformation toughened zirconia. So that is called self matter, zirconia versus zirconia. But in this particular case, we use zirconia versus tungsten carbide cobalt which is hard metal. And here, this cobalt percentage is 6%. So tungsten carbide 6% cobalt that is a typical hard metal that we have used. Now this Y-TZP stands for yttria-stabilized tetragonal zirconia polycrystals.

What it means that, so you add yttria, tetragonal zirconia polycrystals. So essentially the zirconia is yttria stabilized, yttria doped zirconia. The amount of yttria here is typically vary between 2 to 3 mole percent, okay. And Y-tetragonal? Tetragonal means by adding 2 to 3 moles percent yttria to zirconia, we are able to obtain phase pure tetragonal zirconia in this particular case. That means that microstructure is fully tetragonal phase.

What is the linear displacement? is 200 micron, 10 Hz is the frequency and 100,000 cycles is the fretting duration. Why this load? Because we have done that different other initial test but we have found that 8 Newton load is good enough to cause very severe deformation and wear at the fretting surfaces. And this particular combination of parameters also allow us to ensure gross slip fretting contact.

Gross slip fretting contact means if you put tangential force versus displacement, so gross slip fretting contact means it has a very wider loop. And that will give is that larger loop and that is what is expected in many of the applications with severe operating conditions. Testing atmosphere, we have used dry and ambient conditions and then wear is characterized using microscopy as well as laser Raman spectroscopy.

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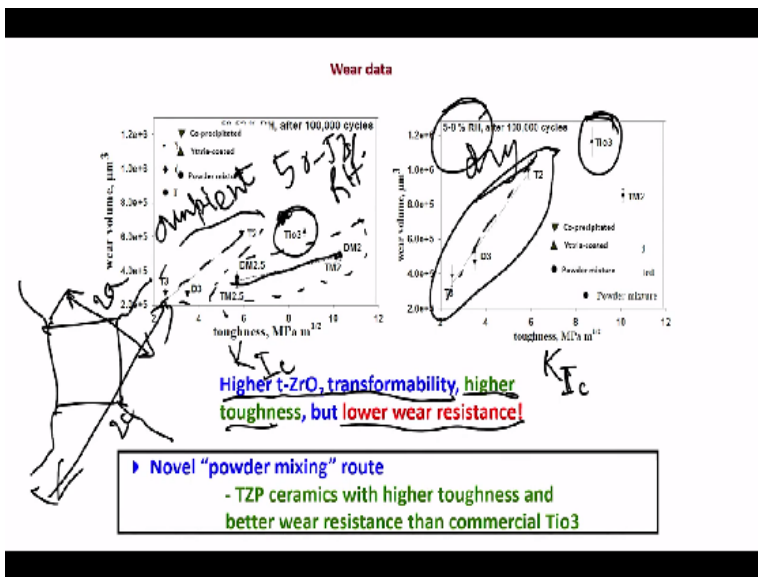
Now this is that ambient humidity conditions you can see. So T3 stands for 3 mole percent Tosoh powders. So it is 3 mole percent yttria-stabilized zirconia and this is also T2 stands for 2 mole percent yttria-stabilized zirconia powders. These are the Tosoh powder. Tioxide, that is another company, this is also 3 mole percent yttria-stabilized zirconia powder, okay. Now intermediate gates TM2 and TM2.5 essentially means that this is the mixed powders of 2 mole percent yttria stabilized and 2.5 mole percent yttria-stabilized zirconia.

Now what you see is that in this particular case, it is 3 mole percent Tosoh powders. The

coefficient of friction of zirconia, this is the Y-TZP versus tungsten carbide cobalt. It is 0.35. It goes up to 0.65 coefficient of friction. That means with commercial powder, coefficient of friction of 3 moles percent zirconia is quite high whereas Tosoh powders are much better. Second important thing is that that when you reduce the dopant content from 3 to 2.5, essentially you are going uphill in terms of friction.

That means frictional coefficient increases. Qualitatively entire frictional behavior is almost similar. But when you come to quantitative differences in terms of the coefficient of friction, steady states (()) (19:19), you see that there is a difference that if you go correspondingly 3 to 2.5 to 2, you see that coefficient of friction is 0.55.

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Now one of the intriguing results is that when you measure that wear volume and when you plot it against fracture toughness, that is fracture toughness is  $K_{IC}$  which is measured using the indentation cracking method here. Indentation cracking means you take a Vickers indent. In case of ceramics, Vickers indent, they cause cracking. Then you measure the total crack length  $2C$ .

You measure the indent diagonal  $2a$  and from there, from this measurements, you can find out that what is the fracture toughness  $K_{IC}$  values. Now what you see that wear volume, then it is increases here as you increase the fracture toughness. That is true for the commercial powders, ceramics which are made from commercial powders.

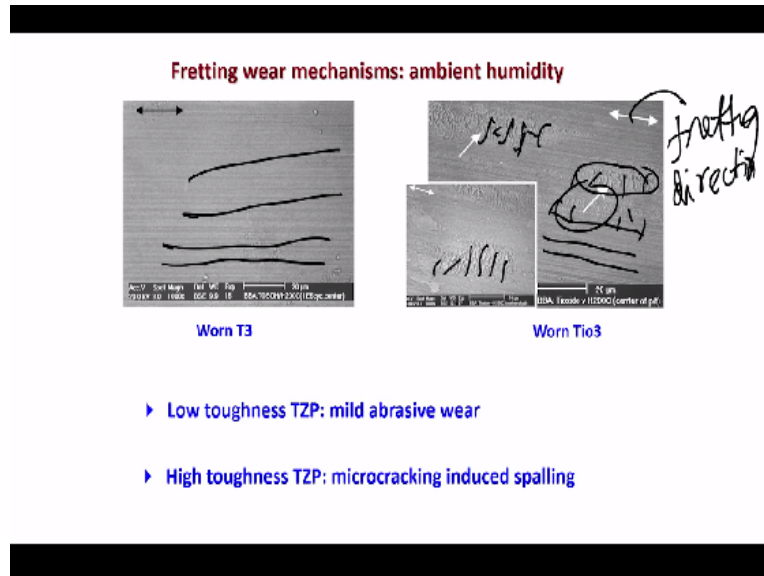
Now from our own powders like powder mixture like TM2.5, TM2 and so on, you again see that there is an increasing trend of wear volume with fracture toughness. This is not only true for 50% to 52% RH that is relative humidity that is ambient conditions. And this is under dry conditions. This is your ambient and this is your dry conditions. So dry conditions again 5% to 8% relative humidity again you see that fracture toughness increases.

From T3D3 to T2 that fracture toughness clearly increases and that leads to increase in the wear volume. So what it means that that it is important to tailor the fracture toughness properties because higher fracture toughness essentially means higher tetragonal zirconia transformability. Transformability means if you go back to my earlier sketches that I have drawn.

So essentially transformability of tetragonal zirconia essentially means that ability of tetragonal zirconia to transform to monoclinic zirconia in the crack tip stress field. So higher the transformability, higher would be the potential of tetragonal zirconia to transform to monoclinic zirconia. This is very important for you to remember that transformability is somewhere similar to hardenability which is used for steels.

So if a steel is very good hardenable mix steel, what it means that steel can be hardened very fast by simple heat treatment conditions, without resorting to very aggressive heat treatment conditions. So higher tetragonal zirconia transformability, higher toughness but lower wear resistance. That is very important because this lower wear resistance that is a concern and that can particularly limit the applications of this zirconia ceramics for various engineering applications.

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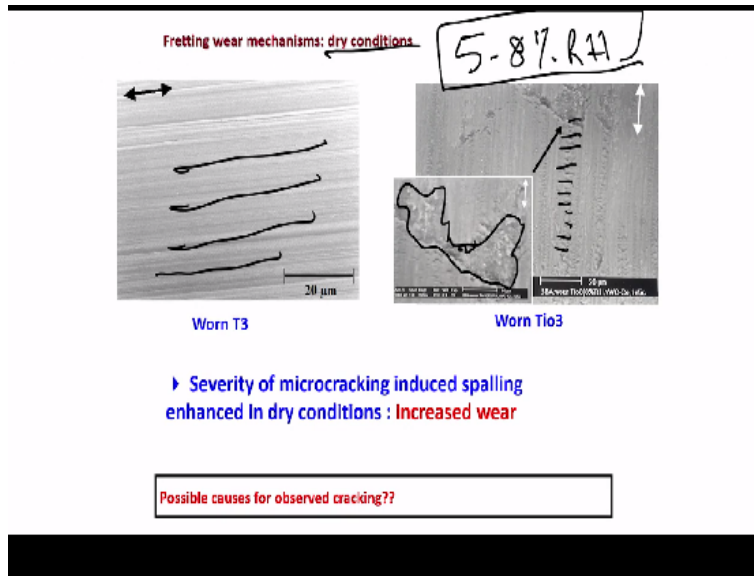


Now if you look at ACN images of the worn surfaces as I have been repeatedly telling in this NPTEL lectures that in this particular lecture, we always emphasize to discuss and describe the wear mechanisms based on various microscopic observations. And so is the case in this present case study that what you see that there is very clear abrasive scratches in that 3 mole percent tetragonal zirconia.

But there are also abrasive scratches, you can clearly see aligned towards the sliding directions or fretting direction here. This is your fretting direction. But what happens is that you will see some additional observations. Now if we look at very closely in this particular image, that there are some cracking. There are some microcracks. And these microcracks are aligned perpendicular to the sliding directions.

And when you align this microcracks perpendicular to the sliding directions, what will happen? This microcracks can grow very fast because in the perpendicular directions, there is also tensile stress field. And your tensile stress field can drive these cracks and that can lead to measurable crack growth and that can lead to microcracking induced spalling. So microcracking induced spalling that is the major culprit for the low wear resistance for high toughness tetragonal zirconia polycrystals.

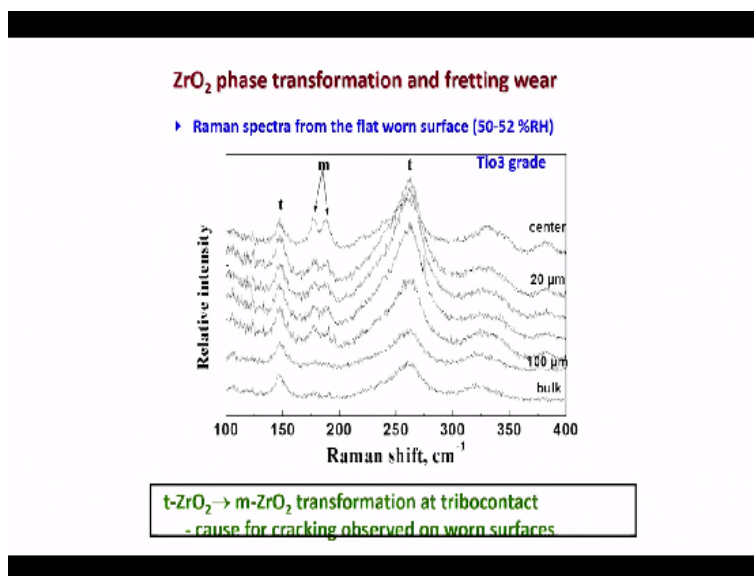
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Now let us look at some other observations. Now what happens in the dry conditions. You remember that we have also done the test as a 5% to 8% relative humidity conditions. Now where the severity of the abrasive scratches increases and that corroborates well with the wear volume of this material. But what is more interesting to see even there is micropacking which is perpendicular to the fretting directions that severity also increased.

And in some of the cases, we have found that there is a very clear sign signature of the spalling. So this spalling is increased at very dry conditions and that leads to increased wear of these materials.

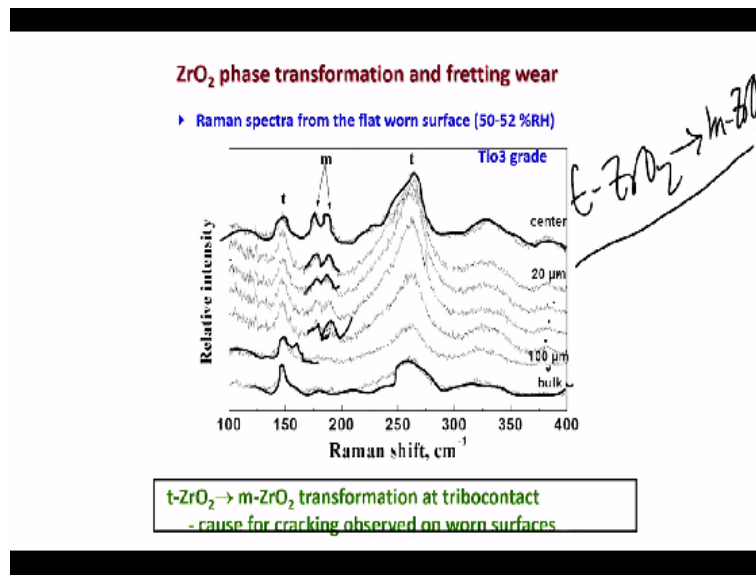
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This is for the very high toughness materials particularly what we have seen in some slides back. This is the tioxide ceramics. So if you go back to this particular slide, I am talking about the wear volume of these particular guys like tioxide ceramic which is one of the company tioxide which is to produce zirconia powder and then we have simply taken the powder and hot pressed it 1450 degree Celsius.

Now in the tioxide ceramic also you can see very clear spalling like a couple of groups of the, abrasive groups are simply spalled off and that is the case for this TM2 that is the Tosoh mix powders and they are again, and that leads to spalling and delamination in this particular case high toughness TZPs.

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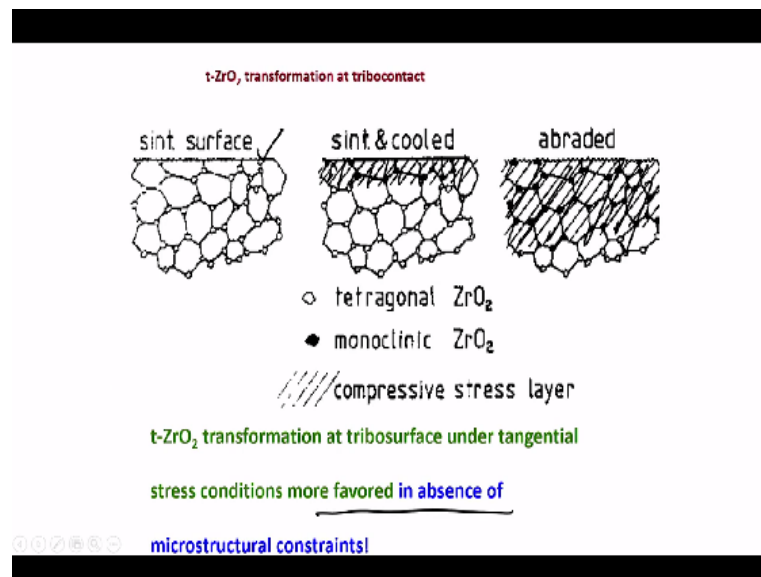
Now as I said before the tetragonal to monoclinic zirconia leads to toughness increase around the crack tip. Now we have observed that there are clear signs of microcracking on the worn surfaces and also the cases where we have observed significant microcracking, that also experiences higher wear or higher material removal or low wear resistance. Therefore, we are interested to know whether this phase transformation also takes place on the worn surfaces.

Now in order to prove that, what we have done? We have taken the Raman spectral from the typical bulk surface and then we have taken at different positions at the center of the worn surfaces where you can see very clear tetragonal band. But also very clear monoclinic band. And

these monoclinic Raman band is also present at various locations from center to 20 micron, 40 micron, 60 micron, 80 micron, 100 micron.

So what it means that at worn surfaces, tetragonal zirconia transforms to monoclinic zirconia, okay and because the phase transformation not only is associated with the volume increase but also associated with the microcracking. Basically crack tips energy is released by the formation and limited growth of the microcracking.

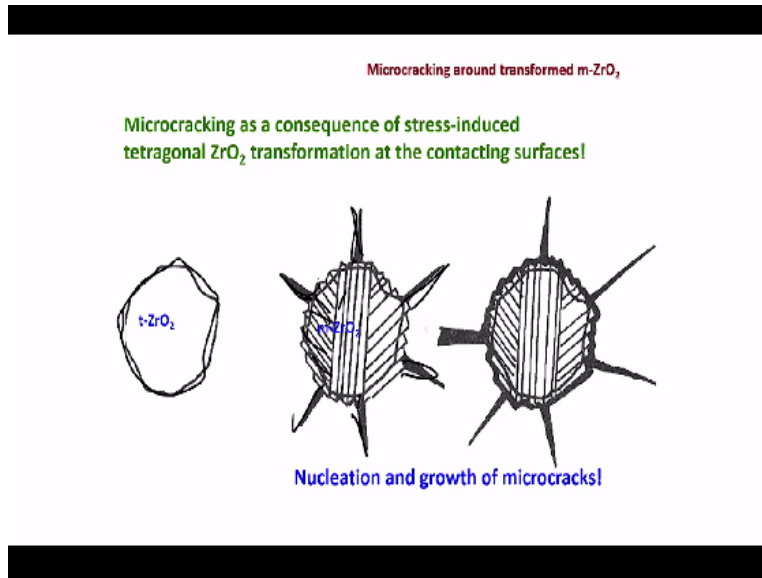
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Now how this microcracking and phase transformation take place? This is, we are trying to explain here with some similar reports from the literature, not exactly it is the same counter body, not exactly under the same testing conditions but also the mechanism, we believe, may be similar. So suppose it is as sintered surface like hot press surface.

It is sintered with cooled, so that means there may be some phase transformation. And when it is abraded, this is that there is a compressive stress layer that is formed. So tetragonal zirconia to monoclinic zirconia phase transformation under tangential stress conditions is more favored in the absence of microstructural constraints.

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And again microcracking around transformation toughened zirconia, you can see this is the tetragonal zirconia and then when it transforms to monoclinic zirconia, then it causes this microcracks which can release from the periphery of the transformed phase.

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Contact stress calculations

► For a ball-on-flat contact configuration, Hertzian contact stress:

$$p(r) = \frac{3Pr}{2\pi a^2} \sqrt{1 - \frac{r^2}{a^2}}$$

Hertzian contact radius,  $a = \left( \frac{3rR}{4E^*} \right)^{1/3}$  where  $\frac{1}{E^*} = \left( \frac{1-\nu_1}{E_1} + \frac{1-\nu_2}{E_2} \right)$

► Maximum Hertzian contact stress in our experiments : 1242.7 MPa

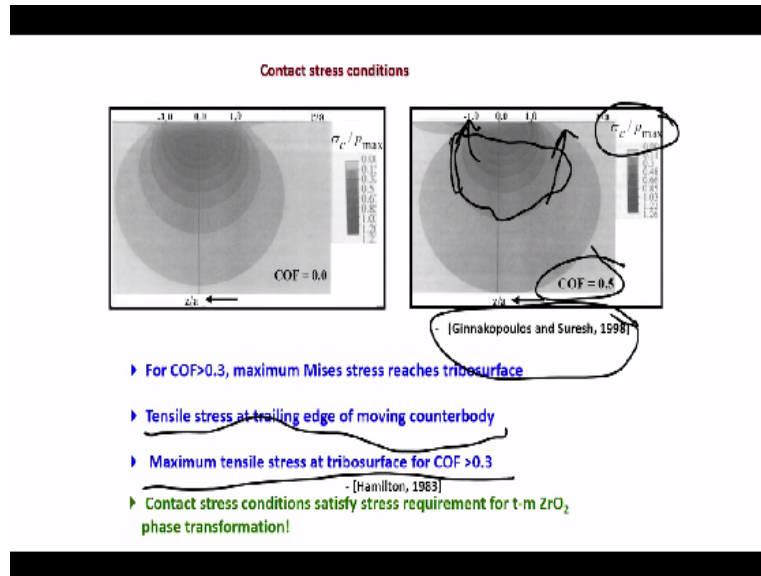
► tangential stress:

$$q(r) = \frac{3\mu P}{2\pi a^2} \sqrt{1 - \frac{r^2}{a^2}}$$

- maximum q (r) at r = 0

One can explain or rationalize this formation of the microcracking by calculating that what is the Hertzian contact stress and this formula you have seen it before. But to repeat, pr is the Hertzian contact stress and then this P is the load, r is any given radius, a is your contact dimension and this is 3Pr/4, you start with the power 1/3 and accordingly tangential stress can be calculated as qr=3mu P/2pi a square square root 1-r square/a square.

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And from there, one can do some calculations and just to show you this is one of the paper, I think, it was published in Acta Materialia in 1998 and then people have shown that group from MIT that Subra Suresh and his group has shown that this is that contact stress region. At the frictional surfaces, 0.5, this contact stress region is shifted. The high contact stress region is shifted towards the tribological surfaces.

And tensile stress is always experienced of the trailing edge of the moving boundary and maximum tensile stress at tribosurface is reached when coefficient of friction is 0.3. So therefore, you have a favorable contact stress environment which can trigger the micropacking in this particular case of zirconia.

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Figure 10 consists of two graphs showing the evolution of wear volume and maximum tangential stress for different materials and conditions.

**Left Graph:** Evolution of wear volume (mm<sup>3</sup>) vs. maximum tangential stress (MPa) for Yttria-coated, Cr-coated, and Powdered nitride materials after 30-92% RH and 100,000 cycles. The graph shows a transition from mild abrasion to induced cracking and subsequent spalling as stress increases.

**Right Graph:** Evolution of wear volume (mm<sup>3</sup>) vs. maximum tangential stress (MPa) for Yttria-coated, Cr-coated, and Powdered nitride materials after 5-45% RH and 100,000 cycles. The graph shows a transition from mild abrasion to induced cracking and subsequent spalling as stress increases.

- And if you put this maximum wear volume with the maximum tangential stress and you can clearly see that this maximum tangential stress increases typically with increase in, and that leads to the wear volume. So it has some kind of correlation. If you kind of follow a trend line, you can see that those ceramics which will experience that higher wear volume also experiences the maximum tangential stress and which leads to tetragonal zirconia phase transformation. So thank you.