

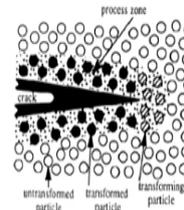
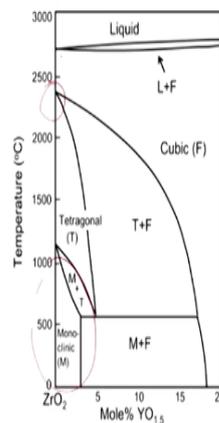
Friction and Wear of Materials: Principles and Case Studies
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Lecture - 28
Wear of YSZ Nanoceramics

So welcome back to this NPTEL course. Today, we would like to see the wear behaviour of yttria-stabilised zirconia nanoceramics.

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Transformation toughened Zirconia



- The addition of small amount of Y_2O_3 can retain tetragonal phase at RT in metastable phase which can transform back to stable monoclinic phase under an applied stress.
- Tetragonal \rightarrow monoclinic phase transformation involves 3-5% volume expansion and introduce compressive stress at the crack tip and restrict the crack propagation

The transformation toughened zirconia ceramics with better toughness and relatively low elastic modulus are considered to be ideal wear-resistant materials for a variety of engineering applications

So we know the zirconia ceramic exist in 3 different crystalline forms, monoclinic at lower temperature up to 1170, and then it becomes a tetragonal at around 2370, and then over that it is cubic, before it gets melted to liquid. So the zirconia, the tetragonal phase or the cubic phase can be stabilised by adding a small amount of yttria. So addition of this small amount of yttria retains this tetragonal phase which is metastable.

So this metastable phase can again retransform into monoclinic under an application of external stress. So this tetragonal to monoclinic phase transformation involves a volume expansion of around 3-5%. So because of this volume expansion and in the strain that introduces compressive stresses at the crack tip. So you can see here, this is a schematic showing the tetragonal phase and then this is transforming to monoclinic and then these are the transformed particles of monoclinic.

So in the vicinity of this crack, there is a transformed zone of monoclinic. So because of this tetragonal to monoclinic, there is a compressive stress generated on the crack. So the crack will not be propagated easily, so you get a fracture toughness improvement. So this transformation, toughens the zirconia. So this transformation toughens zirconia ceramics with higher fracture toughness and relatively low elastic modulus.

These are considered to be candidate material for several wear resistant applications. So today, we considered this yttria stabilised tetragonal zirconia polycrystalline ceramics for their, for the understanding on their wear behaviour. So these ceramics were prepared by spark plasma sintering.

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Spark plasma sintering of Y-TZP

Sample designation	Temperature (°C)	Heating rate (°C/min)	Time (min)	Pressure (MPa)
T3.0-1250	1250	650	5	30
T3.0-1300	1300	650	5	30
TM 2.75-1200	1200	600	5	30
TM2.5-1200	1200	600	5	30
TM2.0-1200	1200	600	5	30

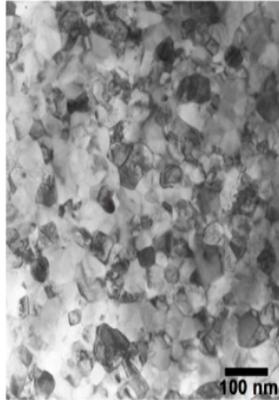
More than 99.5% density

The spark plasma sintering was done with 3 mol % yttria stabilised zirconia. So in these 2 cases, these were co-precipitated, whereas in other 3 cases actually this 3Y-TZP, that is 3 mol % yttria stabilised zirconia with mixed with other powder without having any zirconia to have an overall content of 2.75, 2.5 and 2.0 mol % of yttria. So this investigation was done to understand the effect of yttria on the wear behaviour.

So first 2 samples were done at different temperatures of 1250 and 1300, and then the other samples were done at 1200 celsius with keeping all the other SPS parameters constant. So all these spark plasma sintered yttria stabilised zirconia polycrystalline ceramics, they were of more than 99.5% density.

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TEM image of 3Y-TZP (T3.0)



t-ZrO₂ grains of 70-80 nm size

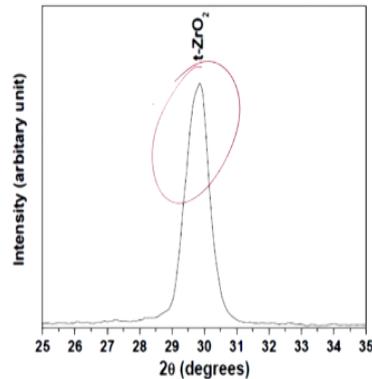
For comparison, average grain size of PS 3Y-TZP 1200C-2 h- (2-200)°C/min: 240-280 nm

So this is the typical TEM image of this 3% yttria stabilised tetragonal zirconia. So you can see all these grains of around 70-80 nanometer grains and for comparison it is to be noted that the average grain size of this pressure less sintered 3% yttria stabilised tetragonal Zirconia polycrystalline sintered at 1200 centigrade for 2 hours, that actually gave around 240-280 nanometers.

So you have a benefit of having a restricted grain growth when these ceramics were prepared by spark plasma sintering. In the spark plasma sintering, so the sintering rates, the heating rates were also high, so more at around 600 Kelvin per minute, whereas at this pressureless sintering these were done at a lower rates of heating. So you get a tetragonal zirconia grains of around 70-80 nanometers and all our XRD analysis also indicate the predominant presence of the tetragonal zirconia.

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XRD analysis



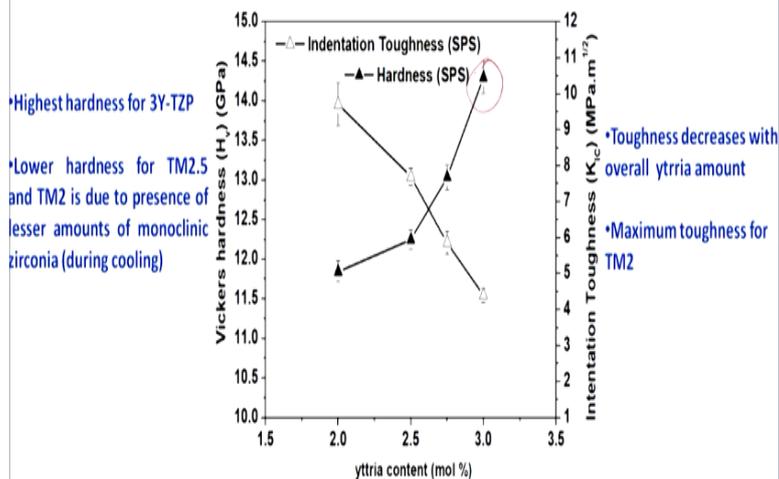
Predominant presence of t-ZrO₂

Peak broadening indicates nanocrystalline microstructure

So we started with the tetragonal zirconia power and the same tetragonal zirconia still retain even after the sintering. But we can also see the peak broadening which indicates nanocrystalline microstructure. The microstructure also shows the grains of around 70-80 nanometers. So with respect to mechanical properties.

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Mechanical properties



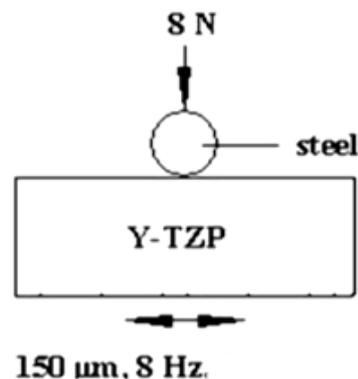
So you can see the function of yttria on the Vickers hardness and indentation fracture toughness. So you can see the hardness vary from around 11.4 to around 14 Giga Pascal with change in the yttria content and the highest hardness is obtained for that having 3% yttria. So this hardness is around 14.4 Giga Pascal for the 3 mol% yttria stabilised tetragonal zirconia polycrystalline, whereas the minimum of around 11.4 Giga Pascal is obtained for that with minimum yttria content of 2 mol%.

With respect to toughness, the fracture toughness gain vary from around 3.9 MPA root meter to around 10 MPA, around 9.5 MPA root meter. So you can see from 3.9 to 9.5 MPA root meter change with the yttria content. So the maximum toughness is obtained for that ceramic stabilised with minimum amount of 2 mol% of yttria, whereas the hardness is obtained for that having the, hardness obtained is lower for that having lower amount of yttria content.

Probably due to the presence of lesser amounts of monoclinic zirconia that may form during the cooling. So having a higher hardness of around 14 Giga Pascal, 14.5 Giga Pascal and fracture toughness of around 9.5 MPA root meter, a combination can be obtained by changing the yttria content.

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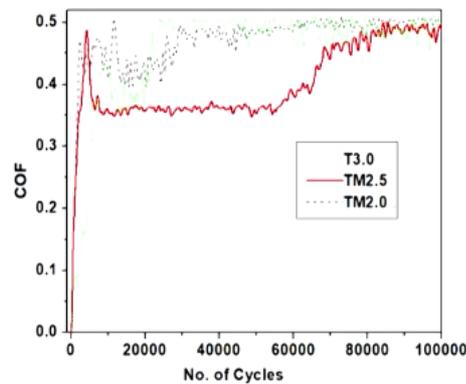
Fretting wear test



So with this information of the material the fretting wear test was conducted for these zirconia ceramics against steel wall. So fretting was done in a mode 1 fretting conditions which gave the gross slip conditions at the contact. So keeping all the parameters constant this fretting is a small amplitude oscillatory sliding movement. The oscillation is around 150 micronmeter, and the frequency of the oscillation was 8 Hertz, and this was conducted for a number of cycles, up to 100,000 cycles.

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Friction results



- COF shoots up to 0.3 – 0.5 within 3000-8000 cycles,
- Subsequently, COF remains constant or goes through a transition before reaching steady-state

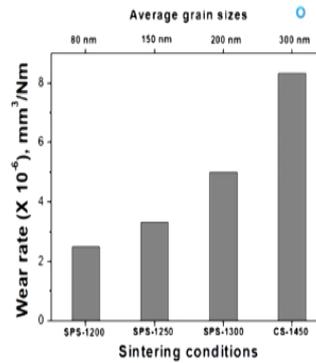
So this is the co-efficient of friction plot against the number of cycles for the investigated ceramics of zirconia nanoceramics with varying yttria content. So you can see initially the co-efficient of friction rises up to a maximum of 0.3 to 0.5 and within the very less number of cycles of 3000-8000 cycles and then there is a transition. So the co-efficient of friction remains constant or it goes actually a transition before reaching a steady state.

So you can also see for the 3% yttria stabilised zirconia it goes immediately after around 20,000, it goes to the higher co-efficient of friction of 0.5, whereas that with the ceramic with the 2.5 mol% yttria, so you can see after reaching the peak state in the running period, it goes to the lower co-efficient of friction around 0.35 and after around 60,000 cycles it, around 40,000-50,000 cycles, it again shoots up and beyond 60,000 it goes to the higher co-efficient of friction of 0.5.

So it actually indicates that the friction is dependent on the yttria content in the zirconia nanoceramic material. So overall the higher co-efficient of frictions were obtained for all 3 samples after around 100,000 of cycles of this fretting against steel.

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Grain size –wear rate



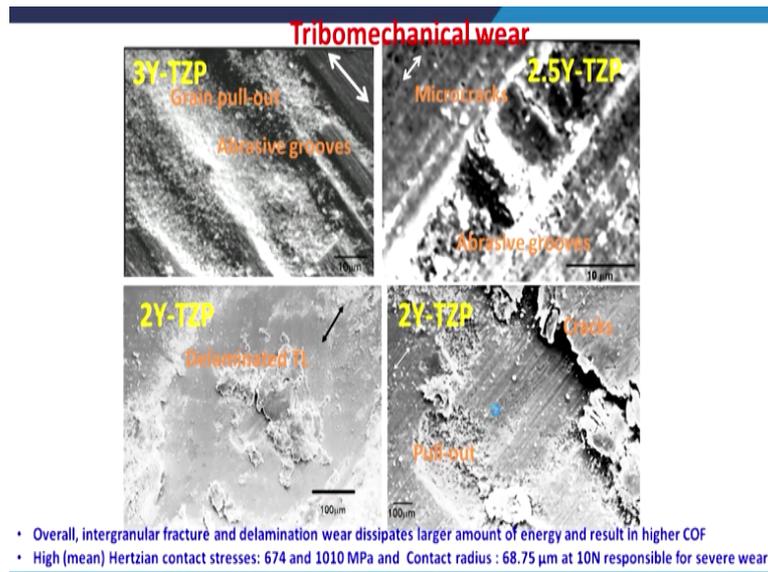
- Less wear in SPS processed samples than in hot pressed (CS) samples of less hardness
- Larger wear for samples with coarser grain size

So the wear rate was determined, the wear rate, you can see the wear rate is very less for the spark plasma sintered ceramics compared to the conventional sintered. For the comparison purpose, these same ceramics having this 3% yttria with, 3% yttria stabilised zirconia, these ceramics are also sintered in hot pressing at 1450 Celsius. So you can see the higher wear rate obtained for the conventional sintered ceramics.

Whereas the lower wear is obtained for the spark plasma sintered ceramics. So in addition to that if you see this with respect to the grain size, the conventionally sintered material has a average grain size of around 300 nanometers, whereas spark plasma sintered have a very less grain size of around 80 nanometers minimum. So it has around 80-200 nanometers average grain size with changing sintering temperature from 1200 Celsius-1300 Celsius sintering temperature, the average grain size changed from 80 nanometers to 200 nanometers.

The wear rate was less for the spark plasma sintered ceramics having a finer grain size, finer grains, whereas the coarser grain material showed a larger wear.

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So let us understand the mechanism of these materials. So you can see the worn surfaces of these ceramics after fretting, they show mainly the mechanical wear. So for example, this ceramic the 3% yttria stabilised zirconia, the worn surface is characterised mainly by the deeper and wider abrasive grooves as well as lot of grain pull outs. So this is mainly because of the mechanical wear, that is characterised by this pull out and abrasion.

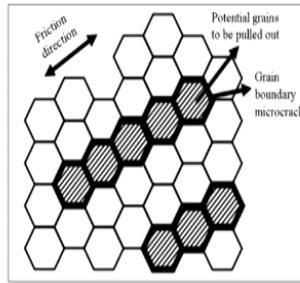
So when the yttria content was reduced to 2.5 again you can see the abrasion grooves and also certain cracks, micro cracks. But when the yttria content was reduced to even lower levels of 2 mol%, there is a change here, so here you can see the delaminated tribolayer here and also in addition to this delaminated tribolayer there are certain cracks and also the pull outs of this material. So overall, we can say the intergranular fracture and the delamination wear, so these dissipate larger amount of energy.

So you get larger co-efficient of friction and wear. So if you can see the Hertzian stress, initial states, the mean Hertzian contact stress vary from 674-1010 MPa and the corresponding contact radius is from 68.75 micronmeter when calculated at 10 Newton load, for this combination of this zirconia, different zirconia ceramics verses the steel material. So you can see such a severe contact stress leads to severe wear.

So there is a change from the grain pull out and abrasion to a delamination of a tribolayer. So let us understand this more clearly.

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Tribomechanical wear



- During sliding, contact stress for 3Y-TZP/steel tribocouple exceeds the critical stress for t-ZrO₂ to m-ZrO₂ transformation
- Microcracks nucleate preferentially at the grain boundaries due to grain sliding and strain incompatibility
- During repeated fretting strokes, microcracks move either through GB or interior of the grain
- Grain pull-out and delamination indicates microcracks move along GB and coalesce to form larger cracks

So what happens during sliding, the contact stress for this tribocouple exceeds the critical stress that is required for the transformation of the tetragonal to monoclinic zirconia phase. So when there is a transformation from tetragonal to monoclinic there is a volume expansion and then there is a microcrack nucleates and the microcrack nucleates preferentially along the grain boundary, grain boundary mainly because of the grain sliding and then their strain incompatibility.

So during continuous fretting, because there is continuous repeated fretting strokes these microcracks either move through this grain boundary or to the interior of the grain. So our worn surface analysis indicates there is a large amount of pull out. Pull out generally happens when the grain boundary is a weaker region and the crack propagates through the grain boundary and the total material of the grain is removed as a pull out.

So it actually indicates the crack propagates through the weaker region which is a grain boundary. So it is schematically shown here because of the repeated fretting strokes, these microcracks propagate through preferentially grain boundary. So the grain pull out happens and of course the delamination of the layer, so the grain pull out and delamination both indicate the microcracks move along the grain boundary and then form a larger longer cracks they coalesce each and then form a longer cracks.

So you can see the cracks also on the, where there is a surface layer, there is a delamination of this layer.

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Tribology of nano ZrO₂

• Two important features:

- Higher hardness corroborates with lower wear rate observed in SPS-processed ZrO₂ ceramics
- Coarser grain size in conventionally sintered ZrO₂ results in large wear rate

The wear damage in nanoceramics is restricted to the central region of the wear pit in case of high-toughness ZrO₂ (TM2). Localized wear, although driven by intergranular fracture, results in less wear compared with conventionally sintered ZrO₂.

So let us understand this tribology of this nanoceramic zirconia ceramics. So there are 2 important features involved in this tribology. Number 1, there is a higher hardness for the SPS processed zirconia ceramics compared to the conventional ceramics. The higher hardness corroborates with the lower wear rate, because it will not allow the wear to happen easily because of the higher hardness.

So the spark plasma sintered materials always show a higher hardness because of the finer grain structure. So the higher hardness agrees with lower wear rate observed for the spark plasma sintered zirconia nanoceramics. The other point is the coarser grain size in conventionally sintered zirconia results in a larger wear rate. So the wear damage in the nanoceramics is restricted to the central region as we have seen here is the central region.

It is restricted to the central region whereas the other region in the contact is more or less smoother region. So the wear is actually confined to the central region of the wear pit in case of the ceramics, particularly those with the higher toughness. So among the investigated ceramics the 2% yttria stabilized zirconia showed a maximum toughness. So because of the toughness, the higher toughness, the wear damage is restricted only to the contact stress, where it has maximum.

The contact stress region is maximum at the central region of the wear pit, so it is localized wear. So such as localized wear although driven by this intergranular fracture results in lesser wear compared with that conventionally sintered zirconia wear.

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Conclusions

- Better wear resistance is exhibited by SPS-processed TZPs in comparison with the conventionally sintered Y-TZP.
- Nanoceramics of varying yttria stabilization level show almost similar frictional behavior with steady - state COF of ~0.5.
- The wear rate lies around 10^{-6} mm³/N.m.
- Tribomechanical wear via intergranular fracture and grain pullout occurs in TZP nanoceramics.
- Microcracking around transforming tetragonal grain boundaries contributes to wear loss of nanoceramics.
- Deeper and wider abrasive grooves are observed on worn 3Y-TZP nanoceramic.
- On the other hand, the wear damage is highly localised at the central region of worn surface on the high - toughness TZP ceramic with overall yttria content of 2 mol%.

So these results can be concluded like better wear resistance is exhibited by this spark plasma sintered zirconia polycrystalline nanoceramics in comparison with the conventionally sintered nanoceramics. Also the nanoceramics of varying yttria stabilization from 3-2 mol%, so these varying yttria stabilization, this shows almost similar frictional behaviour with steady state reaching a maximum of around 0.5.

Whereas the wear rate lies around 10^{-6} mm³/Newton meter for these ceramics with respect to the mechanisms of the material removal basically, the tribomechanical in terms of the intergranular fracture and grain pull out occurs for this nanoceramics. Whereas microcracking around the transforming tetragonal grain boundary that leads to wear loss of the nanoceramics.

So deeper and wider abrasive groups are observed on the 3 mol% yttria added zirconia nanoceramics. On the other hand, the wear damage is highly localized to the central region of the worn surface for the ceramics having a higher toughness, which is in this case, this is 2 mol% yttria stabilized zirconia polycrystalline ceramics. So this particular investigation is very important to understand the effect of the yttria, overall yttria content on the wear behaviour of this nanoceramics.

In addition to that, it also gives an information about the beneficial effect of the nano-sized zirconia, which was processed by spark plasma sintering than that processed by conventional sintering. So the friction in the steady state does not change much, but is always higher

friction because of the rough surface, which is characterized by the intergranular fracture where you have a lot of grain pull out.

As the yttria mole percent decreases to 2 mol%, which results in a higher toughness, so you have a localized wear, so you get a lesser wear comparatively with that observed for the 3 mol% yttria stabilized zirconia. So yeah thank you.