Friction and Wear of Materials: Principles and Case Studies
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Lecture – 35
Erosive Wear of Ultra-High Temperature NbB2-based Ceramic Composites

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Erosive wear of ultra-high temperature NbB_2-based ceramic composites

This is the last lecture on the class of this high temperature ceramics and in this lecture; I will describe the erosion wear of Niobium di boride ceramic.

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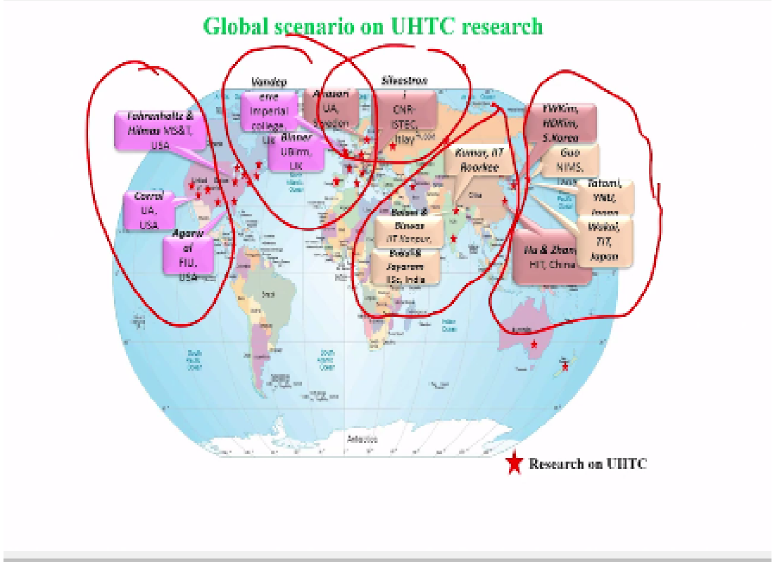

Global scenario on UHTC research

So, like titanium di boride, niobium di boride is also one of the high temperature ceramics and number of groups around the world are working on this high temperature ceramics so that is why what we called global scenario in high temperature ceramics research, you will see in US, it is BILL Fahrenholtz group at Missouri Rolla, Wonder Paris group at Imperial College London and (()) (01:02) and in Europe also in Italy some of the groups are working, in India it is Biswas group and Vikam Jayaram's group at IISc Bangalore apart from the 2 instructors of the present NPTEL course.

And in Japan and China, a host of people are working at NIEMS, Tsukuba, Yokohama National University Tokyo Tech, HIT, China as well as some people in Korea, they are working also in high temperature ceramics.

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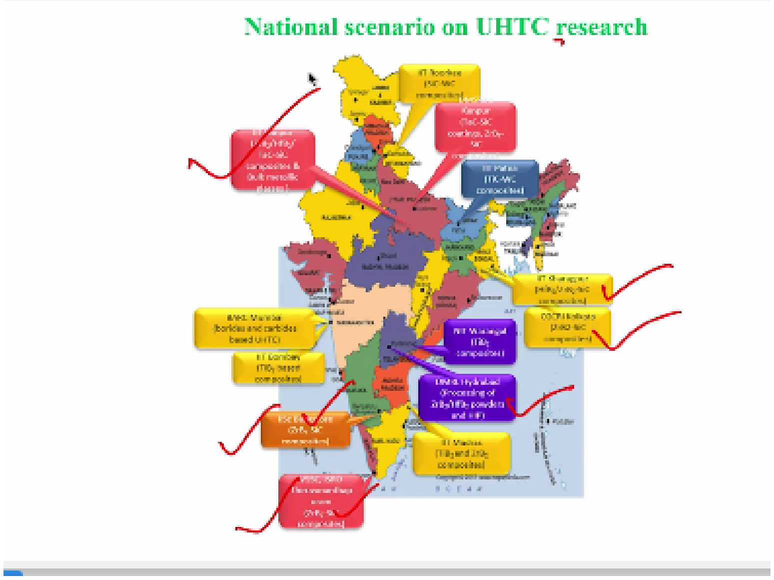

National scenario on UHTC research

So, this is the broad overview of high temperature ceramics in India and as you see that several IIT's, they are working in high temperature ceramics, out of them very few groups are also working on tribology of ceramics particularly, the tribological properties I can mention that VSSC Trivandrum, this is that IISc Bangalore for example, this DMRL Hyderabad, CGCRI at Calcutta, IIT Kharagpur, IIT Roorkee, IIT Kanpur.

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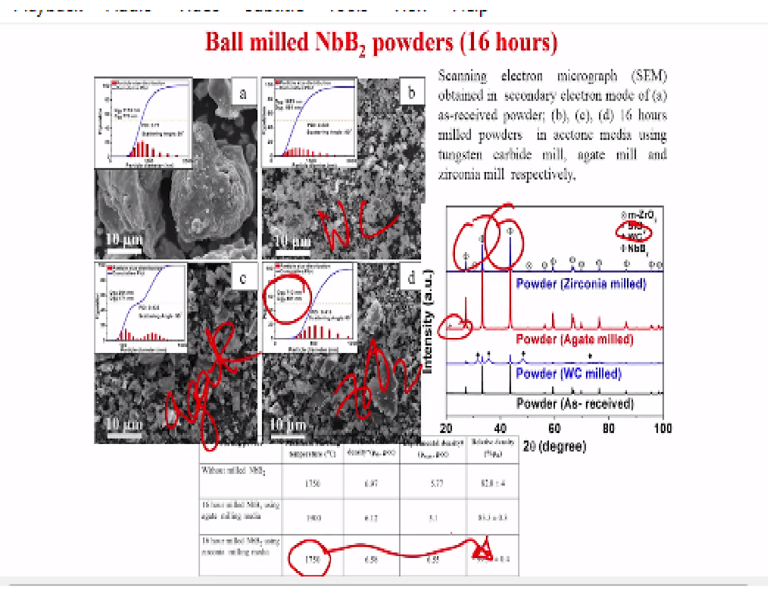

Ball milled NbB_2 powders (16 hours)

Scanning electron micrograph (SEM) obtained in secondary electron mode of (a) as-received powder; (b), (c), (d) 16 hours milled powders in acetone media using tungsten carbide mill, agate mill and zirconia mill respectively.

These are the places where tribology research is currently concentrated, now niobium boride is a one of the member of this transition metal borides and then you can see this transition metal borides this consolidation of transition metal borides like titanium di boride, zirconium di boride, the similar challenges exist also for niobium boride, so first thing is to start with these starting powders in the niobium boride for example, if you can see in the top tunnel A figure, it is that unmilled powder and in the B figure, it is for the B, C, D is it at after ball milling for 16 hours with tungsten carbide.

This is for tungsten carbide, this is for agate, and this is for zirconia, so only in case of zirconia, you see in the D 90, is 7 on 3 nanometer and D 50 is 491 nanometer in agate, apparently the D 50 value is fairly that is 171 nanometer but there is a lot of contamination from agate as you will see later now, if you see X- ray pattern; say X- ray diffraction patterns you will see that the contamination from silica is quite extensive here in the silica.

And then tungsten carbide milling media also, there are small amount of tungsten carbide represent and niobium boride is quite significant in all these cases. Now, as per as sintering and densification is concerned at if 1750 degree Celsius, if you see niobium boride after spark plasma sintering, it is entered to 99.5% sintered density.

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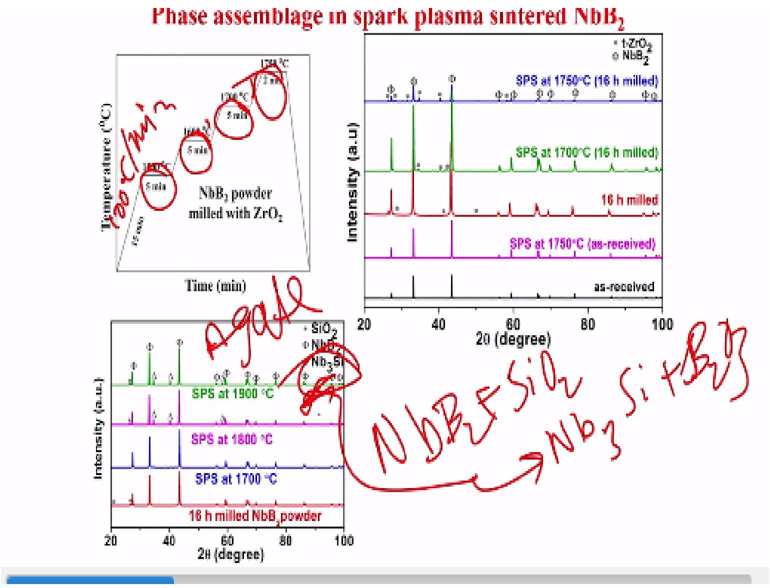

Phase assemblage in spark plasma sintered NbB_2

Now, spark plasma sintering is a technique which is very similar to hot pressing but the fundamental difference between spark plasma sintering and hot pressing here, it is the current that is passing through from the top dye to the bottom dye through the graphite dye punch assembly which contains the ceramic powders and since it is a porous ceramic powders, there are lot of void spaces, now when current is trying to pass through this powder particles.

And if the powder particles are non-contact in that majority of the current will passed to the graphite dye 1, but here some more current would be passing through the powder compact and what happens that in case of the powder compact that void spaces there this current will experience resistance and because of the resistance of heating and Joule heating that locally the temperature will should be very high leading to the higher mass transport that is the internal mechanism of spark plasma sintering of the ceramics.

Now, what is the spatial processing scheme or heating scheme that we have utilised to densify this niobium boride materials, so we heated up to 1500 degree Celsius at 100 degrees Celsius per minute heating rate and then you hold it at 5 minutes, at 1600, we hold it at 5 minutes, at 1700 we hold it at 5 minutes and finally 1750 we hold it for 2 minutes, so it is the force stress sintering or what you call multi stress sintering where the powder compact was held at 1500, at 1600, at 1700 degree Celsius for 5 minutes each.

Before it is held at final sintering temperature at 1750 degree Celsius is for 2 minutes before its cool to room temperature and what you notice here when it is spark plasma sintered at 1750 degree Celsius, this niobium boride with zirconia milk powder you can see there is a clear presence of that tetragonal zirconia but when you use an agate as a ball mill then, what happens there is a second phase than this is apart from silica, there is a third phase called niobium Nb3 Si.

So, what happens; the niobium oxide; niobium more reacts with silica and then it forms is Nb3Si and then also it will form this boron oxide okay, so this reaction accentually take place including in the spark plasma sintering of this materials.

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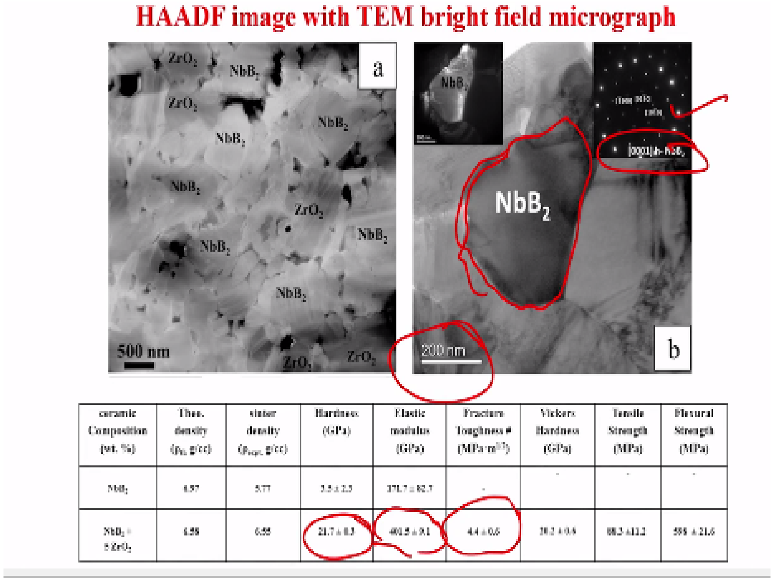

HAADF image with TEM bright field micrograph

ceramic Composition (wt. %)	Theo. density (ρ_{th} g/cc)	sinter density (ρ_{exp} g/cc)	Hardness (GPa)	Elastic modulus (GPa)	Fracture Toughness # (MPa·m$^{1/2}$)	Vickers Hardness (GPa)	Tensile Strength (MPa)	Flexural Strength (MPa)
NbB$_2$	6.97	5.77	3.5 ± 2.3	371.7 ± 82.7	-	-	-	-
NbB$_2$ + 5 ZrO$_2$	6.58	6.55	21.7 ± 0.3	401.5 ± 9.1	4.4 ± 0.6	18.2 ± 0.9	88.2 ±11.2	595 ± 21.6

So, this is that HAADF images, so high angle annular diffraction pattern images TEM bright field micrograph, so what you see here that there are presence of niobium boride and also zirconia faces dispersed in the matrix and there is a equiaxed grains of this niobium boride, if you look at this micron bar, it is roughly around 1 micron in size, so 1 micron or less 1 micron and this is that selected here a diffraction pattern of the hexagonal niobium boride and where it is very clear at this niobium boride boride is retained along with zirconia.

Now, in terms of the different properties for example, sinter density niobium boride has sinter density of 6.55 where theoretically, this is 6.58, it is close to sinter density, hardness is 21.7 gigapascal which is very high, elastic modulus is 4015 +9.1 gigapascal, fracture toughness is 4.4

mp square metre and tensile strength is 88.73, 88.3 megapascal and fissural strength is around 600 megapascal which is this combination of properties, it is not bad.

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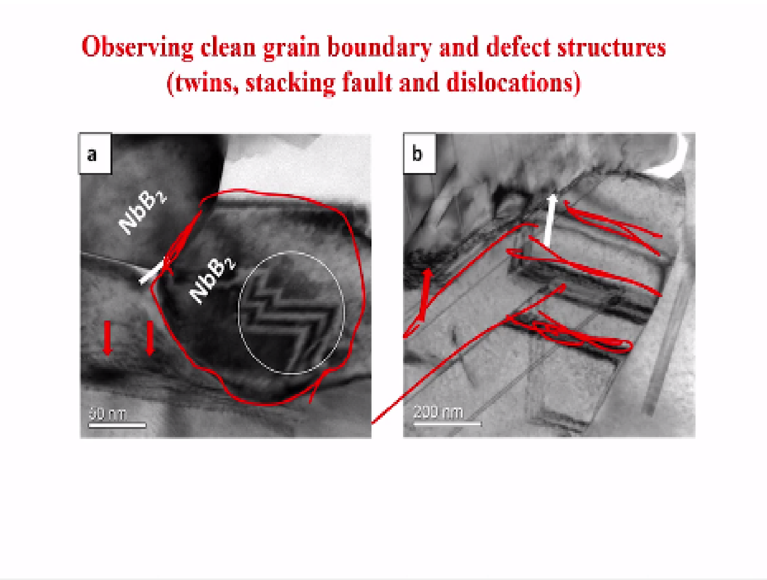

Observing clean grain boundary and defect structures (twins, stacking fault and dislocations)

Now, what you notice here, there is a very clean grain boundaries, so you know clean grain boundaries phases that is also expected and then we have seen the stacking falls and some part of this twins and this are this twins that are intersecting twins are observed in these materials and these are kind of different structures which we have very clearly observe in this niobium boride microstructure.

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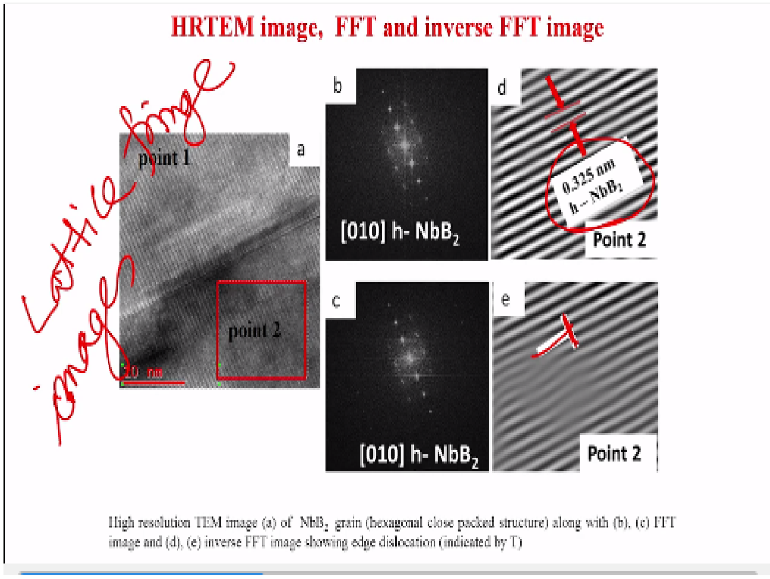

HRTEM image, FFT and inverse FFT image

High resolution TEM image (a) of NbB_2 grain (hexagonal close packed structure) along with (b), (c) FFT image and (d), (e) inverse FFT image showing edge dislocation (indicated by T)

This is the high resolution transmission electron microscope images and this one is essentially called lattice fringe images, so these transmission of the microscopy analysis of ceramic materials just like niobium boride and so on is extremely difficult because the sample preparation itself it takes a lot of time in because one is to have that electron transparent clean film before one can get very decent reasonable and scientifically meaningful transmission to microscopic images.

Now, this left one, if you see this is the bright film clean images and bright film clean images of niobium boride, one can clearly see this lattice fringes, right now, in the right hand side of the images you have, you see that if FT images as well as the inverse FT images and from these FFT images, one can find out that what is the inter planar spacing, in case of hexagonal niobium boride, the inter planar spacing .325 nanometer.

And you will also see a positive edge dislocations while you see the different lattice planes also you will see there is a planar defect like in the terms of the edge dislocations which is a line defect which are also present in this materials.

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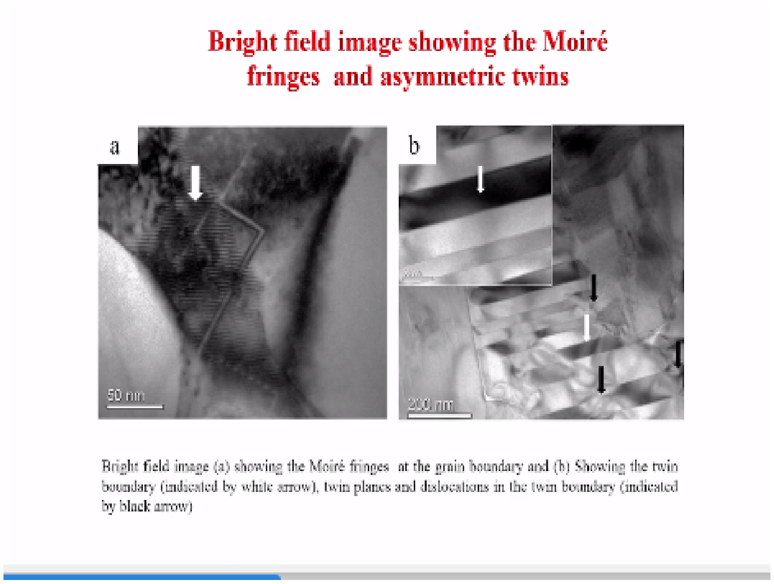

Bright field image showing the Moiré fringes and asymmetric twins

Bright field image (a) showing the Moiré fringes at the grain boundary and (b) Showing the twin boundary (indicated by white arrow), twin planes and dislocations in the twin boundary (indicated by black arrow)

So, this is another bright field images showing the Moire fringes as well as asymmetric twins, so this asymmetric twins essentially indicate that when these materials are heated at high temperature under uniaxial compaction, so essentially deformation twins also generates particularly at high temperature and when it is cool down, so these twins are present across the grains which is the way it should be because once a twins starts, it does not terminate, it should terminate at the middle of the grain unless it is intersected by another advancing twins.

So that is what we learnt in the standard materials and text books and we also observed the same phenomena in case of ceramics.

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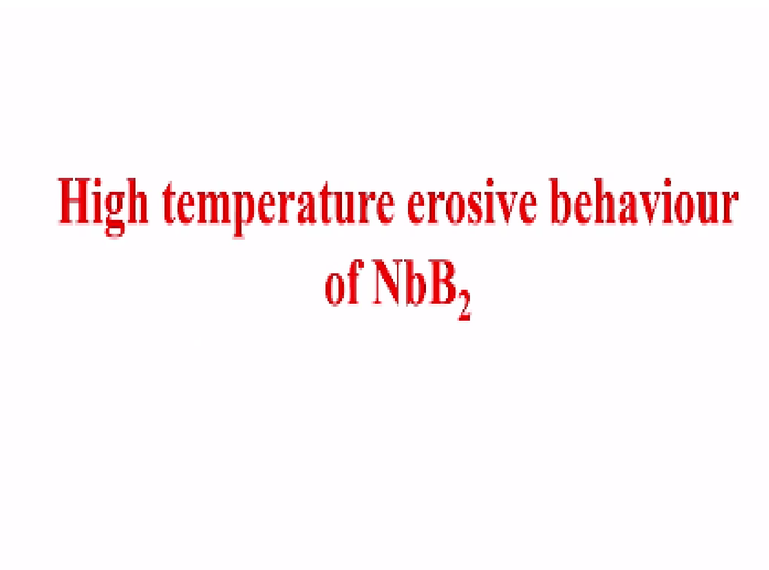

High temperature erosive behaviour of NbB_2

Now, coming to the high temperature erosion behaviour, now before you before I explain you the high temperature erosion behaviour.

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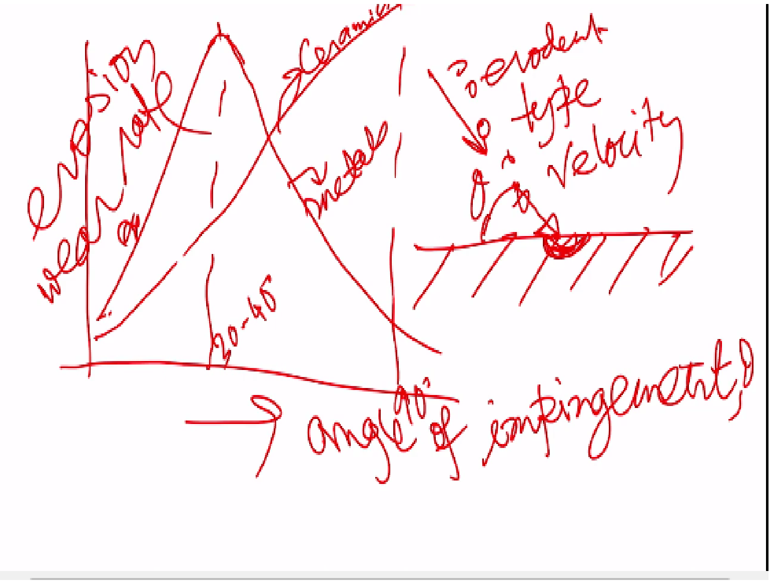

So, erosion essentially means that you have a flat surface, right and you have a erodent particle, so this is called erodent particles, so which will be impinging at an angle theta, right and this what it does is this erodent will strike the material and the stream of erodent's right at a particular speed and these erodent depending on the erodent type and velocity, it is flat material would experience the wear and that will form the crack at sub surface deformation here.

And these particular erosion were loss in case of meters, you can find out by measuring the changes in the weight but in case of ceramics just like any other case of ceramic materials, we use lesser surface profilometer, we take different 2D profiles and we integrate over the distance to get the wear volume, now if you plot the erosion wear rate as a function of angle of impingement that is theta.

Then what happens in case of (()) (12:15) as it goes through a transition at around 30 to 40 degree to theta values and in case of ceramics, then this is for ceramics okay, it goes on increasing up to the angle 90 degree, okay and this is the case for the metals and this is the case for the ceramics, so for ceramics erosion where is maximum at 90 degree, so therefore what is the point that I am trying to make here is that when you do the erosion wear experiments with metals, you should contact these experiments preferably at 30 to 40 degree.

Because one of the major reason behind that because you know that 30 to 40 degree erosion where is the largest or erosion where were goes through maximum and one has to when we develop new materials for wear resistance applications, it is important and imperative to understand there were mechanism and also measure their wire loss at the most aggressive wear conditions as much as possible.

So, from that point of view for ceramics that angle of impingement should be 90 degree for to assess the wear resistance under the most aggressive conditions and that is at the impingement at 30 to 40 degree for metals, although, people too vary the angle of impingement but if you want to do very limited experiments and just to assess the performance under the most aggressive erosion wear conditions then I would suggest you to do it where the wear loss is maximum.

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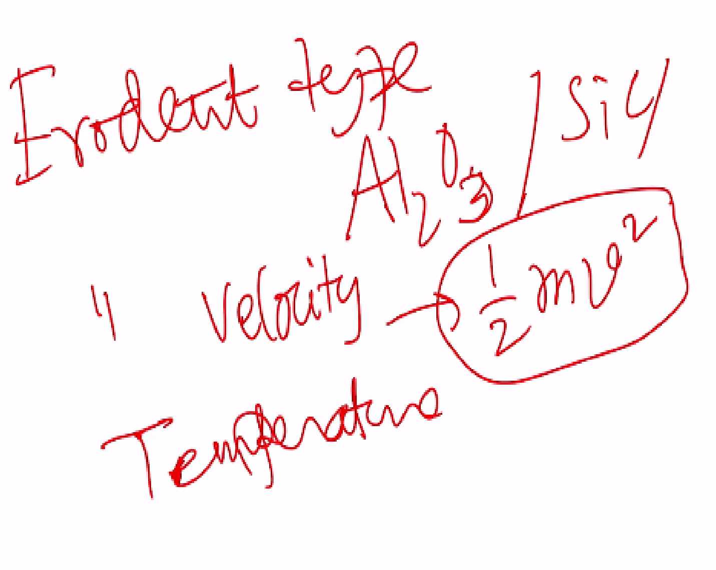

Erodent type

Al_2O_3 / SiC

4 velocity $\rightarrow \boxed{\frac{1}{2}mv^2}$

Temperature

So, what are the different parameters that is important what I said that erodent type, typically the erodent type can be either alumina or silicon carbide, this is at most commonly used erodent, then erodent velocity that velocity at which the erodent is impinging and what is the kinetic energy of the erodent; it is 1/2 mv square, right, so aim is that total mass of the erodent, v is the velocity of the erodent.

So, 1/2 mv square is the kinetic energy and kinetic energy that will be transferred to the material and that can cause either deformation like in case of ductile metals or it can cause fracture in case of brittle materials, so these are the 2 major mechanisms that can be operative under for the 2 different classes of materials, okay and third one is the temperature; temperature means particularly for high temperature ceramics, one must do a erosion study not on a room temperature but also high temperature as high as possible at 800 degree, 100 degree and so on.

Here, I must mention that most of the commercial machines at present are limited in terms of their capability to operate as high as at 1000 degrees Celsius, so there should be a push for all the commercial suppliers to design and develop new erosion wear test, or new tribo tester with their capability to work at 1000 degree Celsius and beyond, so higher the temperature capability more would be our understanding of the high temperature erosion or wear at of different at high temperature ceramic materials.

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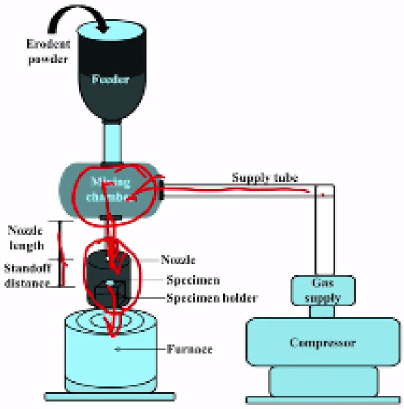
Schematic diagram of erosion set up



Schematic diagram of gas jet solid particle erosion set up

Now, having said this, we have done this experiments in the gas jet erosion set up, this is the schematic of the gas jet erosion set up, so this is the furnace, so you have to keep this entire erosion nozzle as well as specimen's holder inside the furnace here, so this is the typical nozzle length and this is the stand of this test and this is the mixing chamber; mixing chamber is like when you want to use 2 different erodent powders, you can mix it at intermediate layers.

And you can mix also with the gas and through this gas jet, these erodent particles will be bombarding on the material surfaces and it when materials would be experiencing very high temperature and through nozzle, you can also tailor that depending on the nozzle diameter, you can also tailor, you can also allow the amount of the erodent passing through this nozzle diameter, okay.

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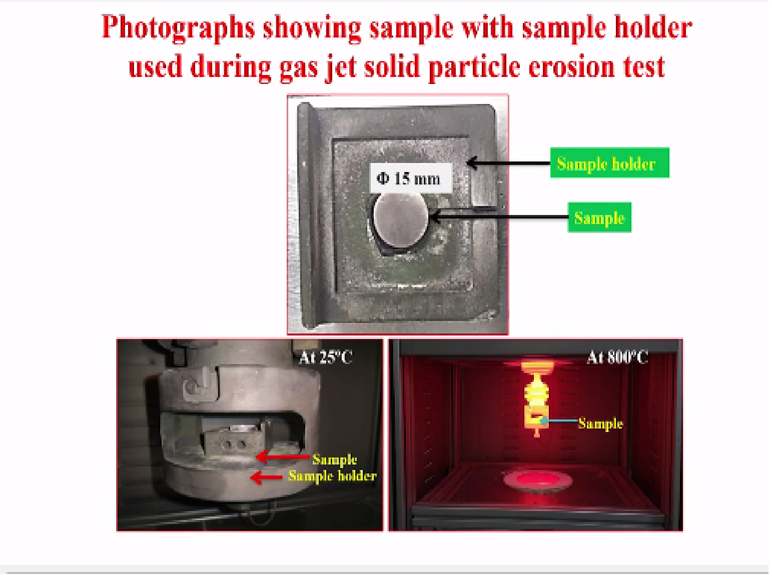

Photographs showing sample with sample holder used during gas jet solid particle erosion test

So, this is that 50 millimeter diameter samples typically, we use that is a top panel you can see the sample holder that is embedded in the sample holder and this is at 25 degree Celsius, you can see through the glass that you know these erosion experiments and when the sample is red hot at 800 degree Celsius, this sample also, this erosion wear is possible erosion experiments can be contacted at 800 degree Celsius as well, okay.

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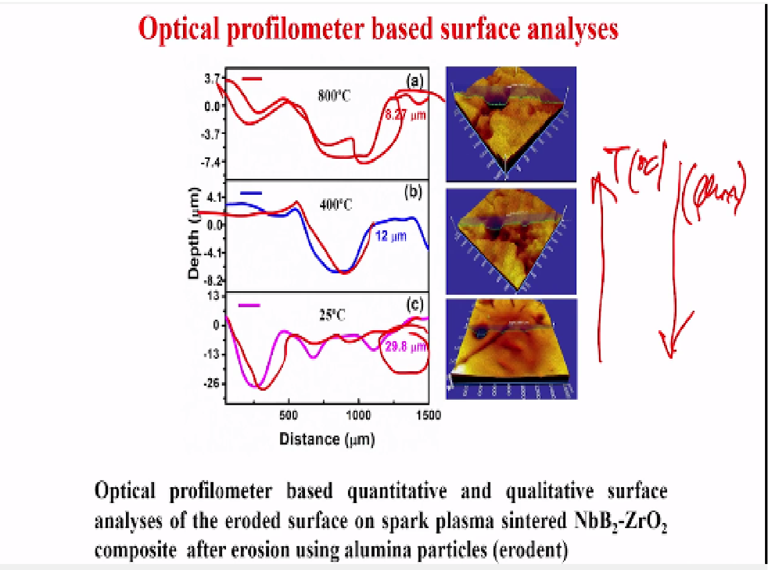

Optical profilometer based surface analyses

Optical profilometer based quantitative and qualitative surface analyses of the eroded surface on spark plasma sintered NbB_2-ZrO_2 composite after erosion using alumina particles (erodent)

This is the optical profilometer based surface analysis, 2D surface analysis at different temperature from at 25 degree Celsius to 400 degree Celsius to 800 degree Celsius and what you notice here in that 25 degree Celsius, it is 29.8 micron in 400 degree Celsius, it is 12 micron and at 800 degree Celsius, it is 8.3 micron, so if you increase the temperature, these temperature is increases of the erosion, if you see that erosion wear depth that micron value decreases.

So, what it means that severity of the erosion damage that decreases as you increase the temperature and this is an extremely important observations because these ceramics are mean to be used for high temperature applications and if this materials can experienced less wear or less erosion damage at high temperature, there is nothing like it and that is how these there is a success in developing this kind of materials with the expectation that these materials will be experienced less wear at higher temperature.

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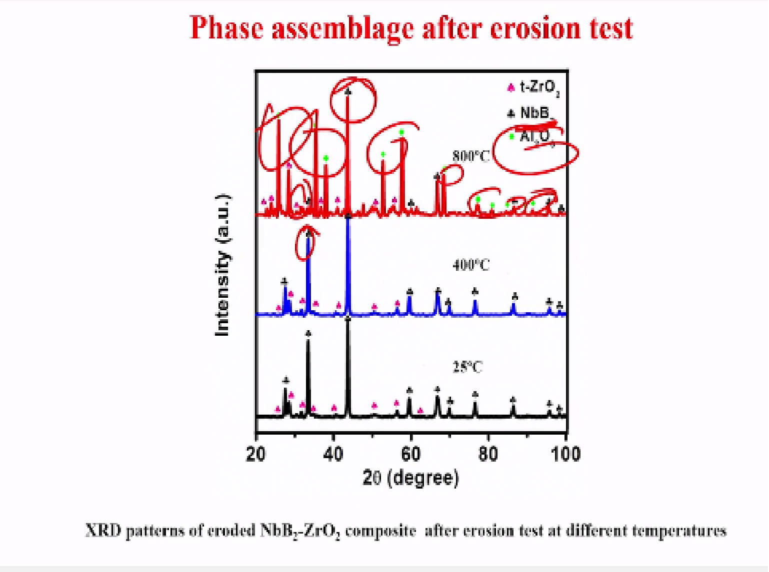

Phase assemblage after erosion test

XRD patterns of eroded NbB$_2$-ZrO$_2$ composite after erosion test at different temperatures

Now, in terms of the phase assemblage after erosion test, what you can see is that this niobium boride materials, this is the niobium boride material and you can see at 400 degree Celsius very clear niobium boride peaks, there is no niobium oxide peak, so niobium boride is extremely resistant to oxidation at 800 degree Celsius, you will see lot of this alumina particles, they are kind of completely embedded on the or covering the surface that is why you will get lot of alumina particles.

So, perhaps that higher the temperature, this alumina particles almost like they are welded on the material surfaces and that is why you are getting this alumina peak very strong and tetragonal zirconia peak that is present in the spark plasma as spark plasma materials and that comes from the milling media for this particular cases.

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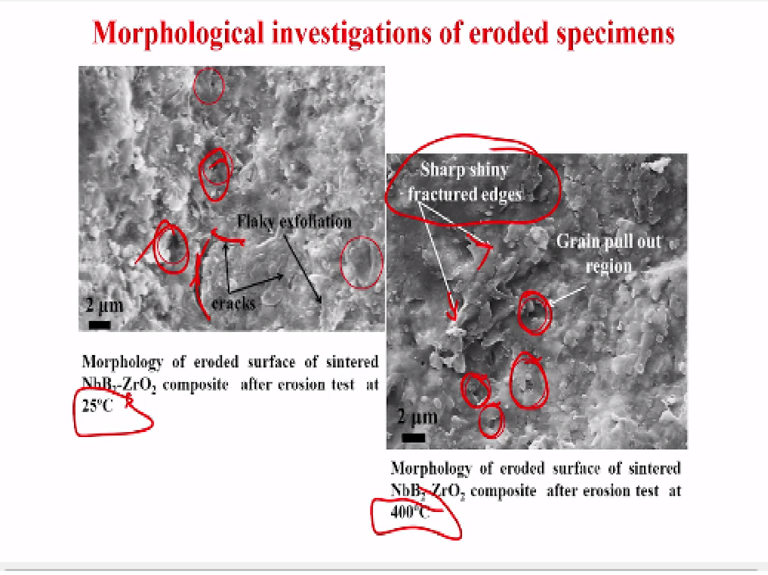

Morphological investigations of eroded specimens

Morphology of eroded surface of sintered NbB$_2$-ZrO$_2$ composite after erosion test at 25°C

Morphology of eroded surface of sintered NbB$_2$-ZrO$_2$ composite after erosion test at 400°C

Now, as I said that as a materials scientist who have great interest in tribology, we are always interested to see how this wear mechanisms, the changes at different temperature right, so this one has room temperature at 25 here room temperature and this one is a 400 degree Celsius, so at room temperature, you can see there are signatures of this flaky exfoliation as well as there are small cracks and these small cracks you can see very easily.

These cracks are present but at 400 degree Celsius after the erosion test is over, you can see there are signature of the poll out, this is the circle the way I am tracing, this is the circle for grain pull out region and there are sharp and shiny fracture edges that are also all clearly observed after testing at 400 degree Celsius.

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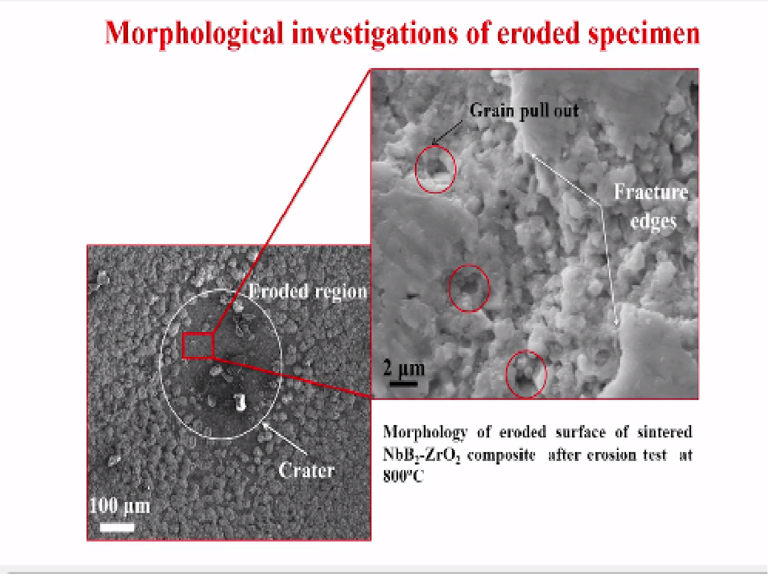

Morphological investigations of eroded specimen

Morphology of eroded surface of sintered NbB_2-ZrO_2 composite after erosion test at 800°C

That 800 degree Celsius you remember that at if you remember that wear rate that at 25 degree, a room temperature, it goes to 4 and 800, the wear depth decreases and what it means that either these alumina particles are covering entire material surfaces and then even after ultrasonic cleaning also, this alumina particles are embedded very strongly and the second thing is that perhaps this at 800 degree Celsius at higher temperature, the ceramic is not prone to brittle fracture anymore.

Because at high temperature there may be signature of some deformation that is possible and that is why this grain pull out and fracture edges, although they are observed but the severity of wear is certainly laser that in the room temperature or 400 degree Celsius.

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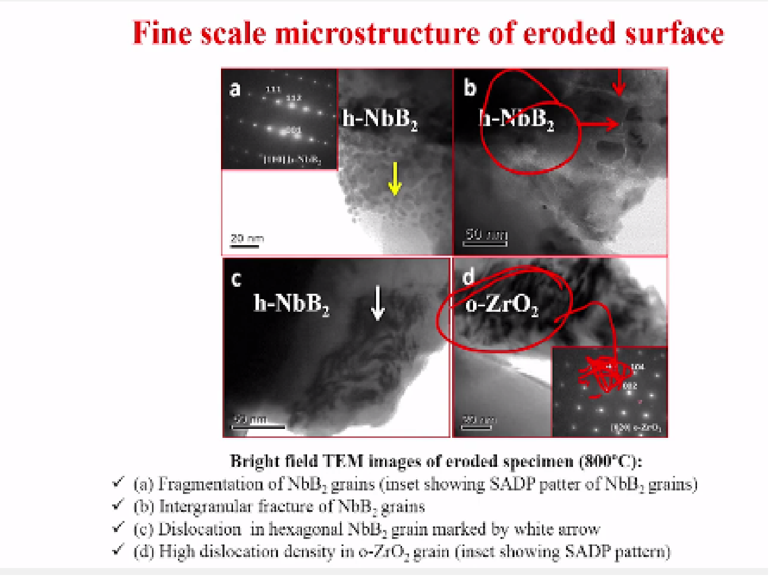

Fine scale microstructure of eroded surface

Bright field TEM images of eroded specimen (800°C):

- ✓ (a) Fragmentation of NbB$_2$ grains (inset showing SADP patter of NbB$_2$ grains)
- ✓ (b) Intergranular fracture of NbB$_2$ grains
- ✓ (c) Dislocation in hexagonal NbB$_2$ grain marked by white arrow
- ✓ (d) High dislocation density in o-ZrO$_2$ grain (inset showing SADP pattern)

Now, what we have done and that is quite interesting is that we have to understand that what is the wear mechanisms in much more with much more clarity, in order to do that we have taken that eroded surface and this that every particles and then we have done very careful TM sample for just we put it in the grid and then we have milled it and then what we have done; we have done the transmission of the microscope images.

What you see that most of the cases, where there is niobium boride is there but there is also orthorhombic zirconia, so these orthorhombic zirconia was not present initially, it was all tetragonal zirconia, as I said we have seen for the cryogenics sliding wear of zirconia but tetragonal zirconia goes to orthorhombic zirconia and before it goes to monoclinic zirconia, when tetragonal zirconia undergoes face transformation, the orthorhombic zirconia is the intermediate phase, so orthorhombic zirconia phases present not only at low temperature sliding conditions; cryogenics sliding conditions.

But also when this material are eroded at high temperature like 800 degrees Celsius again, tetragonal zirconia transforms to orthorhombic zirconia and very confirmatory evidence we have got it from selected area diffraction pattern and this is what you can see here that is a DP pattern of these orthorhombic zirconia.

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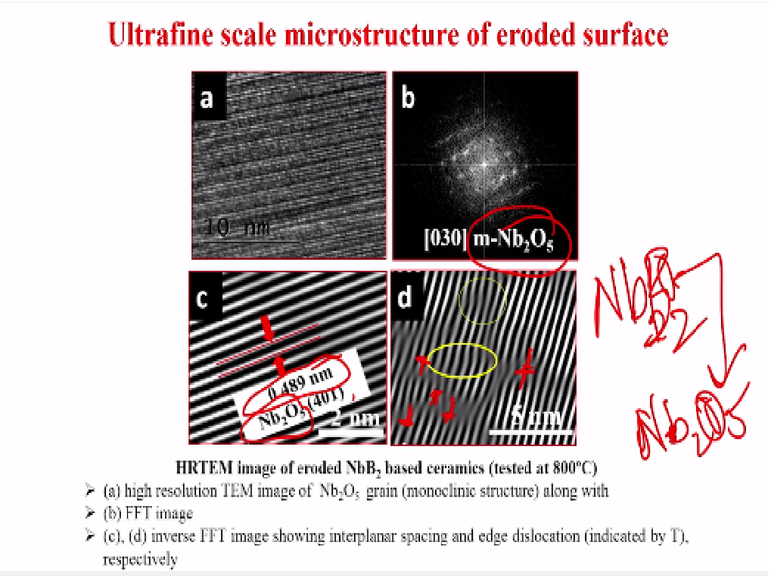

Ultrafine scale microstructure of eroded surface

HRTEM image of eroded NbB_2 based ceramics (tested at 800°C)

- (a) high resolution TEM image of Nb_2O_5 grain (monoclinic structure) along with
- (b) FFT image
- (c), (d) inverse FFT image showing interplanar spacing and edge dislocation (indicated by T), respectively

Now, when you see this eroded surface, in that left hand image you can see the bright field image of these ultrafine scale microstructure eroded surface, the surface scratches and so on and you can see there is also signature of niobium oxide formation now, this niobium oxide formation is so low that one cannot record using x-ray diffraction pattern and there because there the intensity or their amount is much less than what can be detected using x-ray diffraction analysis.

But here what we can see here that in the selected area diffraction pattern clearly shows that Nb2O5 has formed and Nb2O5 essentially is the result of, so niobium oxide; so niobium boride NbB2, it undergoes oxidation to Nb2O5 during the erosion where at 800 degree Celsius and you see that Nb2O5 is a monoclinic phase and this Nb2O5 also lattice phase is 4.489 nanometer and if you look at the right hand images, you see there is a bunch of edge dislocations.

And this edge dislocations are positive and negative these 2 dislocations at some of the places positive and negative edge dislocations that has come together and then they can annealed and they can form a very clear lattice plane.

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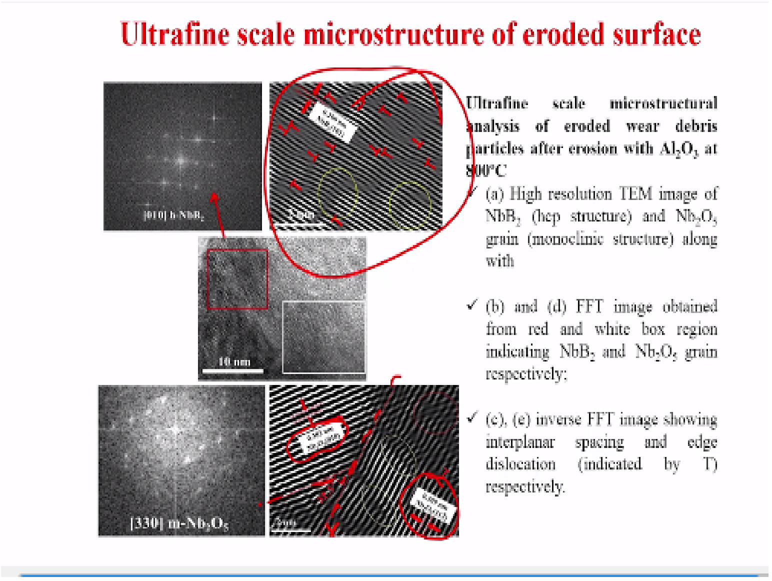

Ultrafine scale microstructure of eroded surface

Ultrafine scale microstructural analysis of eroded wear debris particles after erosion with Al_2O_3 at 800°C

- ✓ (a) High resolution TEM image of NbB_2 (hcp structure) and Nb_2O_5 grain (monoclinic structure) along with
- ✓ (b) and (d) FFT image obtained from red and white box region indicating NbB_2 and Nb_2O_5 grain respectively;
- ✓ (c), (e) inverse FFT image showing interplanar spacing and edge dislocation (indicated by T) respectively.

So, what is the major message that we are getting in these after this erosion; because this is the extremely important observations because we have done this erosion were at different temperature at 400 degree Celsius in 800 degree Celsius and we have done this careful transmission electron microscopy image analysis and what is most interesting that whatever we are not able to detect using x-ray diffraction or scanning electron microscopy.

When we do transmitter microscopy, we are able to see all those signatures like NbB2 undergoes oxidation to Nb2O5 grains that is because of the erosion, you also see the lot of dislocation activity in these eroded region essentially, saying that these are the signs of dislocation plasticity which is taking place at high temperature leading to the reduction in the wear damage wear induced damage.

So, this presence of this multiple dislocations, if you look at this particular micrograph you know that in this kind of images for the Nb2O5 grains, it is extremely fascinating to see that this particular grains is this Nb2O5, these are the 2 grains, here the along the 313 or plane, the inter planar spacing is .309 nanometer and here, 010 plane here the Nb2O5, the inter planar distance is .382 nanometer.

So, in this particular range, you can see that there is also there are lines along this line this edge dislocations and this edge dislocations essentially a present entire the signatures of the dislocation activity in this materials of the eroded surface so, all in all this combination of the dislocation activity as well as Nb2O5 phase formation essentially indicates this erosion experiments at 800 degrees Celsius causes measurable oxidation.

And also noticeable dislocation activity and it is quite possible that dislocation plasticity reduces the wear of this materials because dislocation plasticity in contrast to micro cracking induced pollings which commonly takes place in the case of a brittle ceramic, so these are 2 things that is may be important in this particular case of ceramics.

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