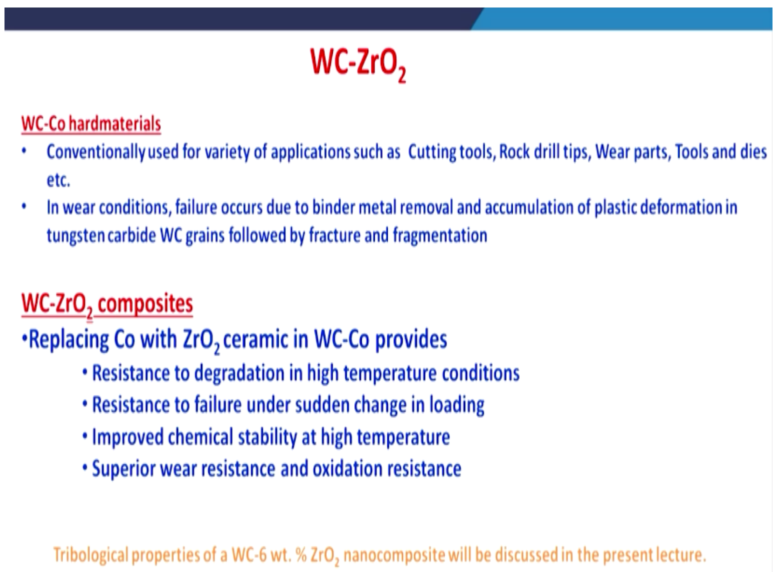
Friction and Wear of Materials: Principles and Case Studies
Prof. B. Venkata Manoj Kumar
Department of Metallurgical and Materials Engineering
Indian Institute of Technology – Roorkee

Lecture - 29
Wear Behavior of Nanostructured WC-ZrO2 Nanocomposites

Hello, welcome back. So in this lecture, we will try to understand the behavior of tungsten carbide zirconia nanocomposites in tribological conditions. So generally tungsten carbide based hard materials are used for varieties of applications such as cutting tools, rock drill trips, wear parts, tools and dyes and metal forming dyes, etc.

(Refer Slide Time: 00:57)

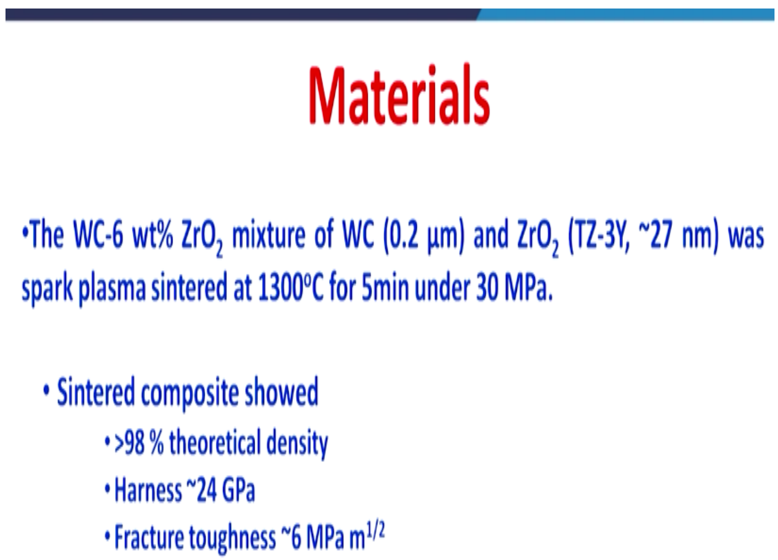


So in the wear conditions, the failure of this tungsten carbide based materials, particularly the tungsten carbide cobalt hard material occurs due to mainly binder material removal and then the fracture and fragmentation of the ceramic material. So if we can replace this metal binder of cobalt with zirconia ceramic, so we can have an improved resistance to the degradation in high temperature conditions.

Those are generally possible in high cutting tool applications and also we can have an improved resistance to failure under sudden change in the loading or we can have improved chemical stability at high temperatures because the system of the zirconia steel is chemically stable at high temperature than the cobalt or the steel and in turn we get a superior wear resistance and superior oxidation resistance.

So mainly the degradation of the material in terms of the metal binder removal and/or by the fracture or fragmentation can be reduced if you go for a ceramic additive than the cobalt binder, but the tribological properties of that tungsten carbide having zirconia composite is not understood thoroughly. So in this lecture, we will see the key results obtained for the tribological behavior for a tungsten carbide 6% zirconia and nanoceramic composite.

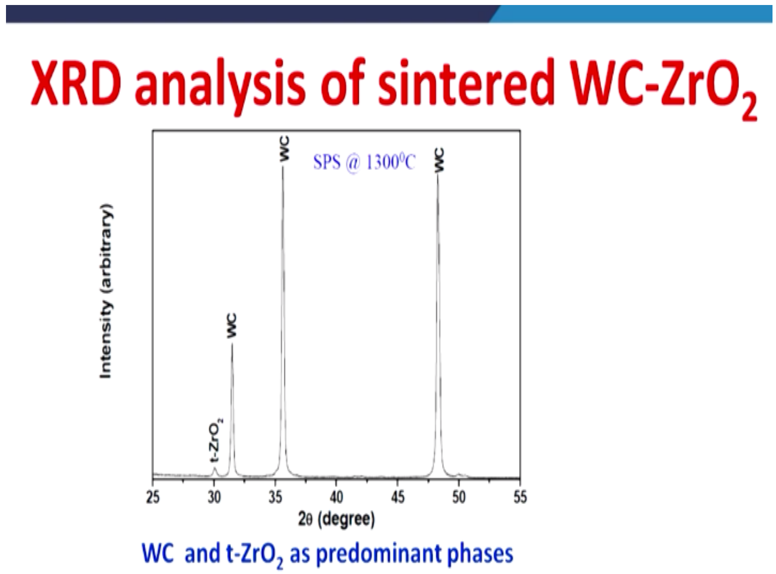
(Refer Slide Time: 02:48)



First of all, the tungsten carbide of around 0.2-micron meter and the zirconia which is a tetragonal zirconia, which was stabilized by 3% yttria. So 3-mole% yttria stabilized zirconia powder of around 27 nm. So these 2 powders tungsten carbide and zirconia are mixed in a tungsten carbide 6% zirconia powder mixture and this mixture was a spark plasma sintered at 1300 celsius for 5 minutes under 30 MPA pressure with high rates of heating of around 600 Kelvin/minute.

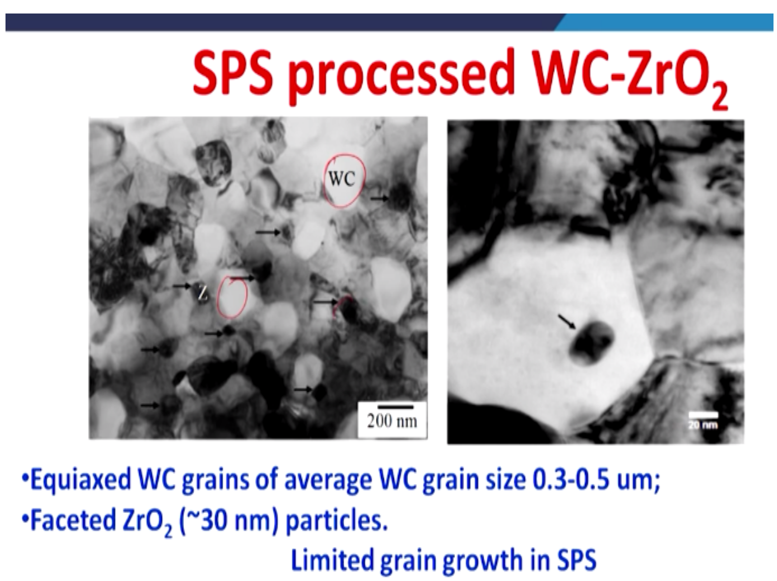
And all these ceramic composites, they showed a very high density of more than 98% of the theoretical density and then also showed a hardness of around 24 gigapascal and the fracture toughness of around 6 MPA root meter. So the tungsten carbide cobalt material generally has a hardness of around 11-12 gigapascal whereas such tungsten carbide zirconia has an extremely high hardness of around 24 gigapascal. Of course the fracture toughness is moderate with 6 MPA root meter.

(Refer Slide Time: 04:06)



So the sintered tungsten carbide zirconia ceramic composite was investigated for the phase analysis and the microstructural characterization. The phase analysis by x-ray diffraction technique indicates the predominant phases of the tungsten carbide and tetragonal zirconia. So there is no other phase formed as well as no change from the tetragonal to monocline zirconia during sintering. So this shows the efficiency of the sintering technique we used, that is spark plasma sintering.

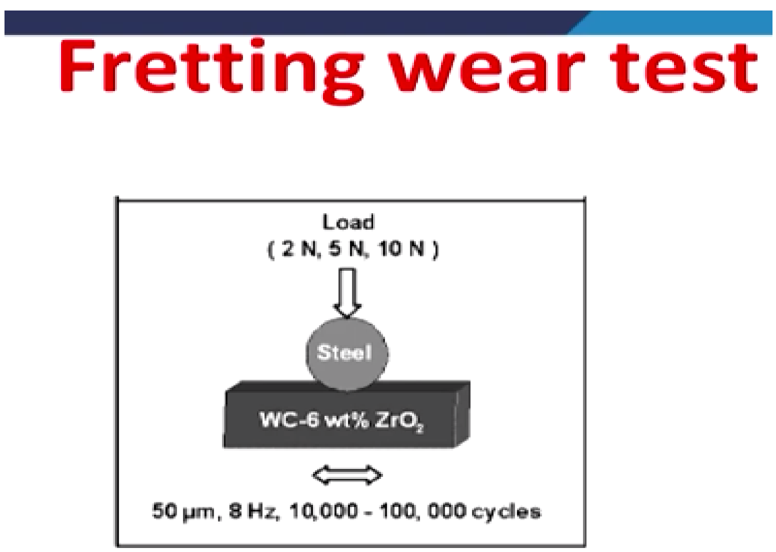
(Refer Slide Time: 04:38)



So the spark plasma tungsten carbide zirconia ceramics, they showed a microstructure of equiaxed tungsten carbide grains and then the zirconia particles along the grain boundary as well as inside the grain of this tungsten carbide. So the equiaxed tungsten carbide grains have an average grain size of around 0.3-0.5 micrometer whereas the zirconia particles are still within the nanoregion, those having around 30 nm.

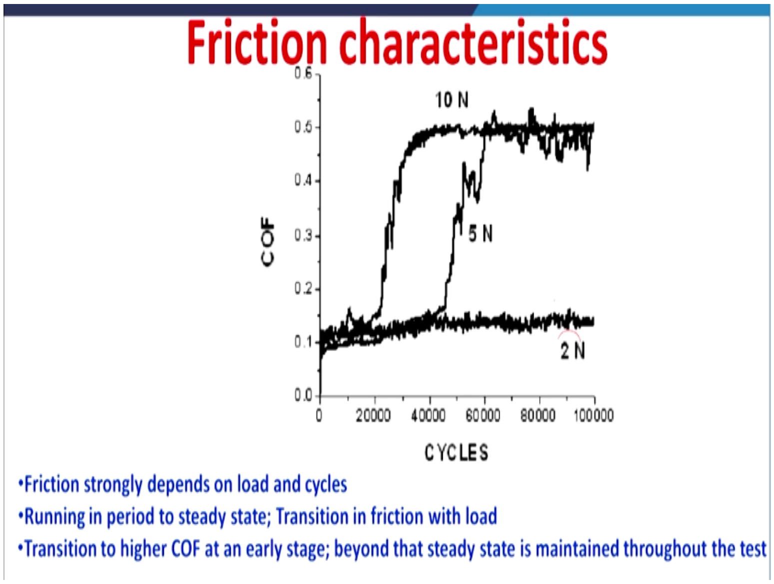
So considering the initial particle size of around 0.2 micronmeter for the tungsten carbide and around 27 nm for the zirconia. So this sintering technique is efficient to have a dense material of tungsten carbide zirconia ceramic with a nanoregion of zirconia particles distributed in a grain structure of the tungsten carbide. So there is a limited grain growth occurring in this spark plasma sintering, which is going to give a combination of superior properties.

(Refer Slide Time: 05:49)



So that is how we got very high hardness of around 24 gigapascal and a moderate fracture toughness around 6 MPA root meter. So these materials, the tungsten carbide 6% zirconia ceramics were fretted against steel at a different loading conditions with a fixed combination of the fretting parameters. These fretting was done in a mode 1 fretting conditions which again gave a gross slip condition at the contact. So the fretting test parameters were fixed at 50 micrometer oscillation displacement with a frequency of 8 hertz.

(Refer Slide Time: 06:40)



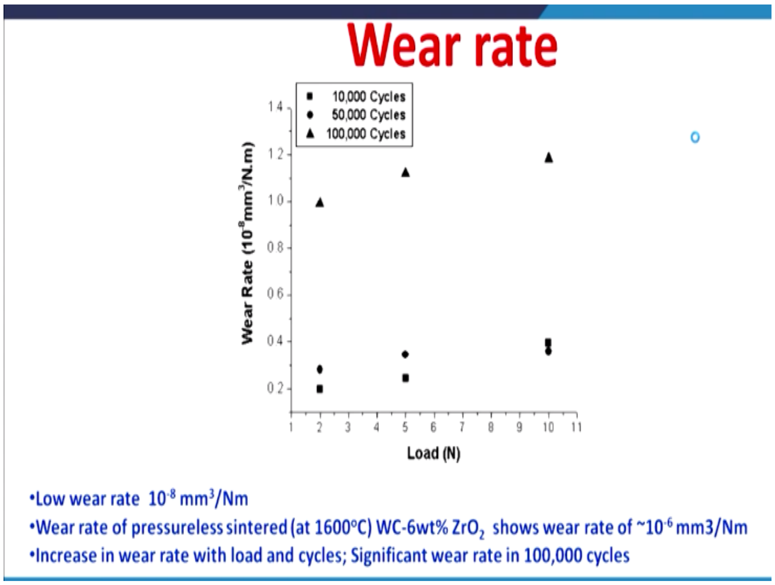
And then the fretting was conducted with varied numbers of cycles from 10-50-100,000 cycles. So let us understand the frictional characteristics as a function of the fretting duration as well as the load applied. So this fretting shows the friction is strongly dependent on the both load as well as the numbers of cycles. So at a lower load, the friction goes to a very less coefficient of friction around 0.1 and around 20,000 cycles and then remains almost same throughout the test up to 100,000 cycles.

There is no change in the coefficient of friction whereas as the load is increased to 5 Newton, the friction coefficient is around 0.1-0.15 in the initial 20,000 cycles and as it reaches the 40,000 cycles, it actually shoots up under by around 60,000 cycles it goes to the maximum coefficient friction of 0.5. So there is a transition with the fretting duration for the test done at 5 Newton load and if you can see the test done at the 10 Newton load, you have the transition occurring even at an early stage.

So the coefficient of friction was less in initial stages of around 20,000. Immediately after 20,000, it went up to 0.5 average coefficient of friction in the steady state and this reaches around 40,000 cycles. So always there is a running in state and the steady state. No much difference running in state coefficient of friction and steady state coefficient friction at lower load, whereas there is a difference in the running in state coefficient of friction and the steady state coefficient of friction at higher loads.

In addition to that, we saw a transition occurring from low load to higher load in the friction. So the transition to higher coefficient of friction occurs at an early stage for the test done at higher load and once it achieves the steady state, it actually remains in the steady state throughout the test.

(Refer Slide Time: 09:06)



The wear rate was also determined. So you can see the wear rate varying from around 0.2, 10 power –8 mmQ/Newton meter to around 1.2 mmQ/Newton meter. So there is a change in the wear rate with change in the load as well as the numbers of cycles of this fretting. First of all, the wear rate is of 10 power -8 mmQ/Newton meter. So this is a very low wear rate as you compare with the wear rate obtained with the conventionally sintered tungsten carbide 6% zirconia ceramic.

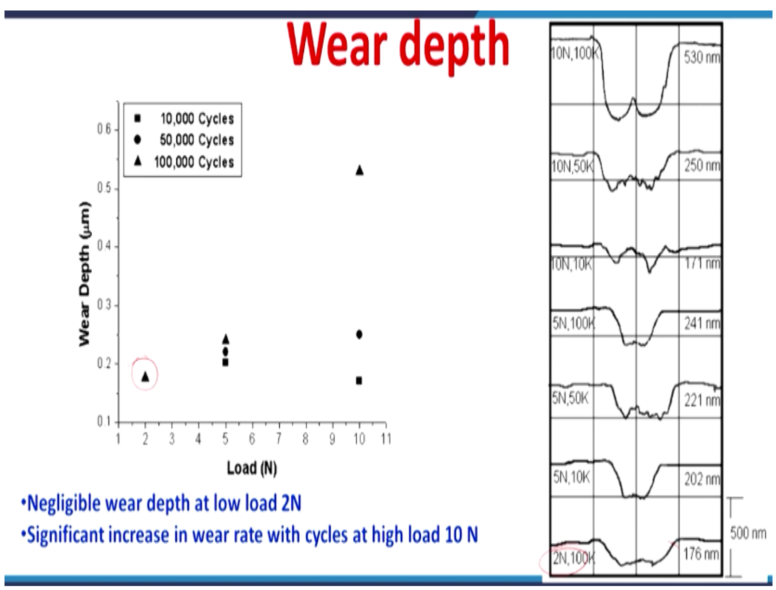
So this shows 10 power –6 mmQ/Newton meter whereas the spark plasma sintered tungsten carbide zirconia, nano ceramic composite exhibited a wear rate of 10 power –8 mmQ/Newton meter. So increase in wear rate is also observed with increase in the load as well as the cycle. Now at a lower load, if you see, at a lower load, the wear rate was less for the test done for the small numbers of cycles that is 10,000 cycles.

For the test done at 10,000 cycles, even if you change the load, there is no much difference. So it actually changes from around 0.2 to around 0.4*10 power –8 mmQ/Newton meter. Now if you see the 50,000 cycle result, again at lower load, the wear rate was less and it actually increases and then almost same at 10 Newton load. So again there is a small increase with the load, but after 5 Newton, there is no much difference.

But if you look at the 100,000 cycle test, at lower load itself, the rate was very high almost 1000 magnitude higher than that obtained for the 10,000 cycles test. So it actually increases monotonically with the load. Highest wear rate is obtained for the test done at 10 Newton load for 100,000 cycles. So this particular information indicates that the wear rate varies with the load as well as the fretting duration.

Similar to that we observed for the friction. Friction also changes with the load or the fretting duration. So the wear depth also indicates very important information.

(Refer Slide Time: 11:52)

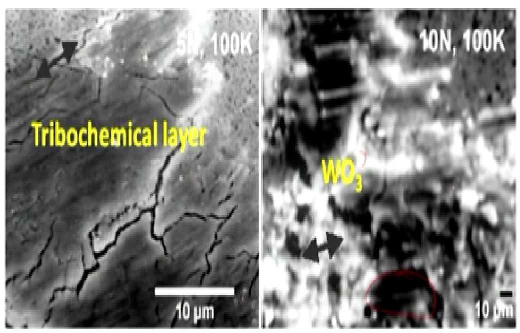


There is a negligible wear depth at lower loads of 2 Newton, but a significant increase in the wear depth as well as the wear rate at the higher loads of 10 Newton. So let us study worn surfaces to understand the mechanism of the material removal for the tungsten carbide zirconia nanoceramic composites. At a lower load of 2 Newton, you can see the wear scar is very much smoother and a high magnification image of the same surface shows there is a mild abrasion. There is an abrasive groove. So you have an abrasion, which is mild at lower load of 2 Newton.

So it is also agreeing with the information we obtained with the wear depth. The wear depth is negligible at 2 Newton load after 100,000 cycles, whereas at higher load actually the worn surface shows a significantly different characteristic than that obtained at the lower load. At higher load, the worn surface is mainly covered by a layer and the layer is different in the contrast than the worn surface that indicates there is a chemistry difference in the layer.

(Refer Slide Time: 13:17)

Tribochemical wear at high load

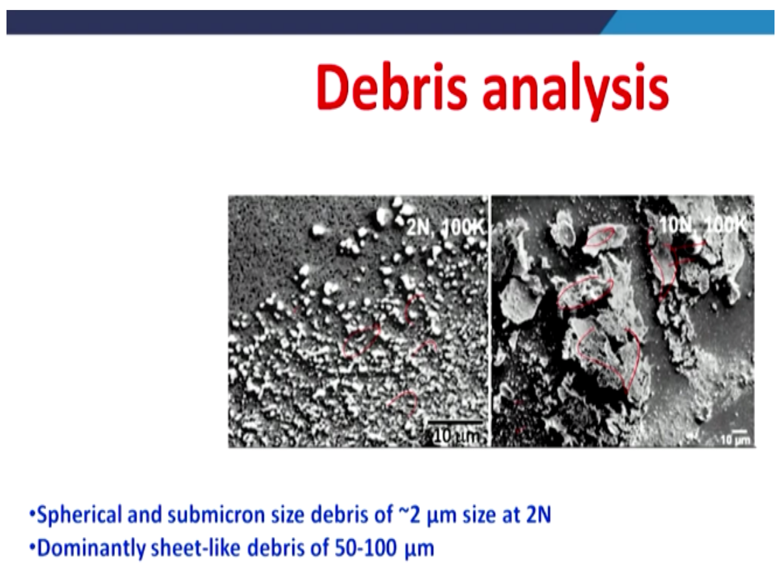


And you can see with increasing load again this chemistry difference, the contrast difference increases and again if you can see there is a black region, a white region, and a bit grey region. A black region is a normal worn surface and then the white region is mainly rich with the heavier elements than the grey region. So it is believed that this grey region has an iron and then iron oxide or the white region a bright contrast shows a tungsten oxide rich layer.

So we will also confirm these with the other EDS and other analysis. Now these surfaces also indicate, the tribolayer is severely cracked. The severe cracking of this tribolayer indicates it is non-protective in the nature. So when the tribolayer is non-protective, it actually cracks and then the underneath surface is again subjected to further wear. So if at higher load of 10 Newton, the more pronounced cracking is observed after this 100,000 cycles.

So tribochemical wear is dominant at higher loads that is 5 Newton or more than the 5 Newton. So at lower loads, it is mild abrasion and at higher loads of 5 Newton or more, it is a tribochemical layer formation and then removal that we call at a tribochemical wear. So there is a change from the abrasion to the tribochemical wear with change in the load in these studies. So the debris are also collected and then the debris analysis also shows there is a striking difference with respect to load.

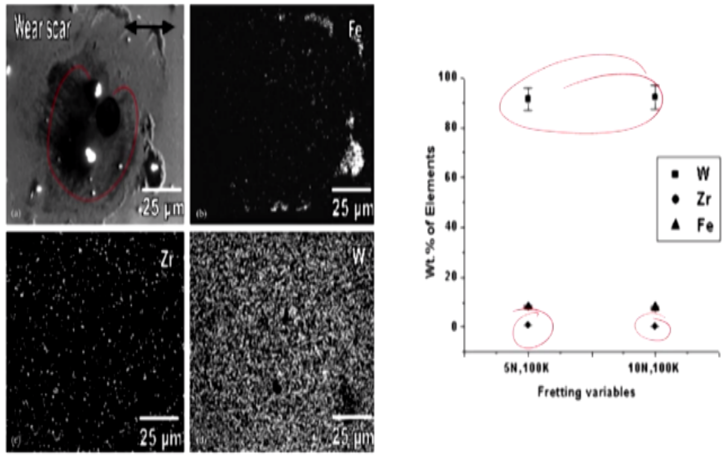
(Refer Slide Time: 15:21)



With a lower load, you can see the debris of very small size, whereas at increased load of 10 Newton you can see the dominantly, the debris are of the sheet like or plate like debris with a larger size. Of course there is a smaller debris here, but predominately there is a sheet like debris and the sheet like debris is around 50-100 micron meter whereas the small size debris, which is observed after fretting at lower load of 2 Newton is around 2 micron meter. So there is a change in the size of the debris as well as the shape of the debris with respect to load.

(Refer Slide Time: 16:04)

EPMA of tribolayer



The EPMA analysis of the tribolayer indicates this tribolayer is rich with the tungsten. So you can see the tungsten rich tribolayer, of course there is an iron also present, but it is a tungsten rich tribolayer.

(Refer Slide Time: 16:28)

High wear resistance of ceramic nanocomposites

Two important factors: High hardness and Fine microstructure

- High hardness
  - Higher hardness (~24 GPa) lead to lower COF and wear – only realized at low load of 2N
  - Low wear depth
  - Material damage restricted to submicron region below the wear surface
  - As load increases from 2 to 5 N, transition in friction and wear
    - At low load, mild abrasion
    - At higher load (5N or more), tribochemical wear

So let us understand the wear resistance of the ceramic nanocomposites, 2 important factors have to be considered. Number 1 the high hardness and the number 2 fine microstructure. The higher hardness, which is extremely hardness obtained for this nanoceramic composite around 24 gigapascal, the higher hardness lead to lower friction and wear, but these are observed only at a lower load of 2 Newton.

At lower load, there is a very, very less wear and characterized by the low wear depth. It is less than 1 micronmeter. The material damage is restricted to submicron region below the worn surface whereas at higher load as the load is increased from 2 to 5 Newton, there is a transition in the friction and wear. At lower load, there was a mild abrasion whereas at higher load that is a 5 Newton or more, the tribochemical wear dominates.

With respect to the finer microstructure obtained by this spark plasma sintering for this nanoceramic composites. At lower load of 2 Newton, you found fine debris, the fine debris particles necessarily indicate the pull out of tungsten carbide particles. The tungsten carbide particles and once these are pulled out, these tungsten carbide particles are subjected to fracture. So these are called by the repeated fretting strokes.

And once these pulled out tungsten carbide particles are in the contact, where this fretting is continuing in ambient conditions, there is a possibility for the oxidation. So the pulled out tungsten carbide particles are oxidized into tungsten oxide. So we can infer that there is a mild oxidative wear occurring at the contact at a lower load of conditions of 2 Newton, whereas at higher load, 5 Newton or more, these oxidized debris form a tribochemical layer.

The tribochemical layer is rich with the tungsten oxide or iron oxide. So once these tribochemical layers rich with the tungsten oxide or iron oxide is stabilized, the contact is actually between the steel ball and the layer not between the steel ball and the tungsten carbide zirconia surface. It is actually between the friction is happening between the steel ball and the layer. So because of that you get higher coefficient of friction.

So we can also understand the transition in the wear mechanism by studying the debris size. So in lateral fracture modal, the minimum load required to produce the fracture because of the point contact is dependent on the fracture toughness, hardness values.

(Refer Slide Time: 19:34)

Debris size and wear mechanism

$$P^* = \frac{54.47\beta}{\pi\eta^2\theta}\left(\frac{K_{IC}}{H}\right)^3 K_{IC}$$

P* is the minimum load required to produce fracture from a point contact
β the constant relating hardness to diagonal (2.16 for Vickers Indentation), η is a constant, θ the geometrical constants (≈ 0.2),
K_{Ic} the fracture toughness of the material indented and H the hardness of the material indented

S.G.Roberts. Sci. Mater. 40 (1) (1999), 101-108.

Minimum load required for fracture due to abrasion: ~2.15 N

Ejection of few debris from the contact and three body abrasion leads to lower friction and wear rate at low load !!

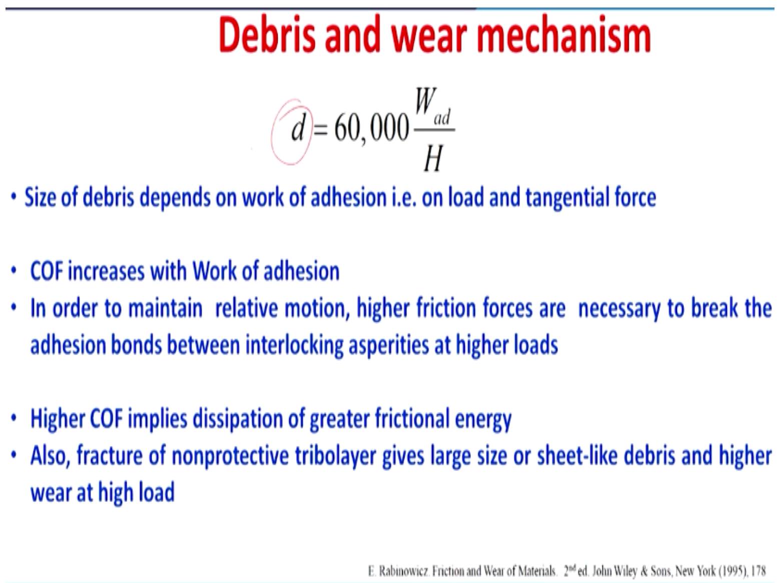
So these robot has explained that the minimum load required can be determined if you know the fracture toughness and the hardness for the Vickers indentation. So in this formula, the beta is a constant relating to the hardness to diagonal. Generally, for the Vickers indentation, it is 2.16 whereas these constants of eta and theta are taken as 0.2 and then we can get this minimum load required for the fracture to obtain where there is predominately abrasion.

And the minimum load required for such an abrasion induced fracture is around 2.15 Newton for the investigated ceramic composite. So as we have seen, there is an abrasion predominately mild abrasion happening at a lower load of 2 Newton. So it is quite possible that a lower load of 2 Newton such a fracture is initiated and then the removal of the material occurs by the abrasion. So once these material is removed as debris, these debris are trapped in the contact and few of them may go out of the contact.

So few of the debris may be ejected out of the contact. So that leads to a lesser coefficient of friction and also because of these debris in the contact, it actually is a 3 body abrasion. The 3 body abrasion that means, these particles will be able to roll easily, so it gives a lesser wear. So all these at lower load of 2 Newton, you got a minimum load of 2 Newton that is sufficient for the fracture to occur.

Once this fracture occurs, the debris particles are in contact and few of them ejected out. So that leads to lower coefficient of friction and because of the easy rolling it actually gives lesser wear as well. Whereas in case of a higher load, we saw there is a tribochemical wear dominating. So the tribochemical wear actually resulted in a sheet like debris of a larger size of around 50-100 micronmeter, so we can also understand this with the adhesion theory.

(Refer Slide Time: 22:13)



The size of the debris can be actually related to the work required for the adhesion to happen. So the work of adhesion that means the load as well as the tangential force. So we can actually see the coefficient of friction involvement here. In fact, the coefficient of friction increases with the work of adhesion. So larger the amount of work of addition more will be the coefficient of friction.

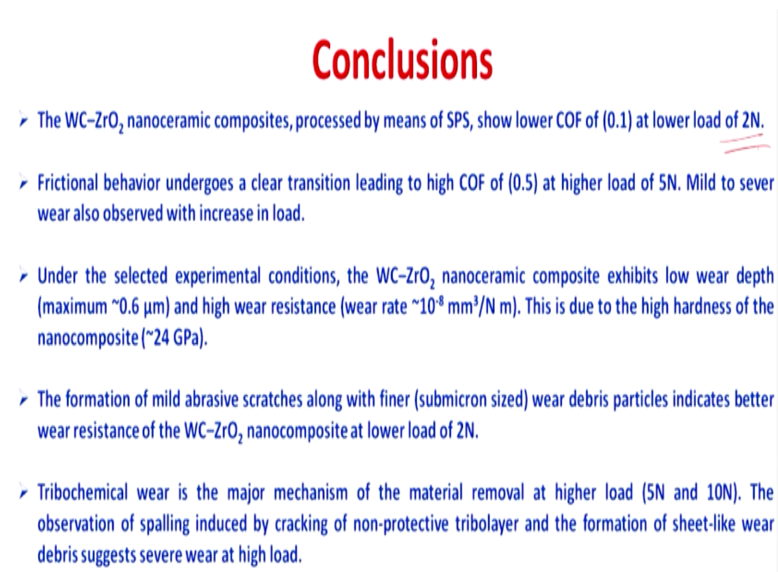
So in order to maintain the relative moment, higher frictional forces are necessary to break the adhesion bonds between the interlocking asperities at the higher loads. So higher coefficient of friction implies dissipation of a larger frictional energy, also the higher coefficient of friction and wear can also be understood by the non-protective tribolayer nature. So we have seen the tribochemical layer formation and then their cracking that indicates the non-productive nature.

The non-protective tribolayer is fractured and gives the larger sized or the sheet like debris and correspondingly higher wear at a higher load. So these 2 mechanisms of the abrasion occurring at a lower load as well as the adhesion and then the corresponding tribochemical wear occurring at the higher load can be understood right from the debris size. So these 2 mechanisms can be understood from the debris size.

So concluding the results obtained in the wear behavior of the tungsten carbide zirconia and nanoceramic composite in a fretting conditions against to steel lower coefficient of friction around 0.1 is absorbed at lower load of 2 Newton whereas frictional behavior undergoes a clear transition leading to higher coefficient of friction around 0.5 at higher load of 5 Newton are more than that.

Mild abrasion to severe wear of tribochemical layer formation and its delamination is observed with the increase in the load from 2 Newton-10 Newton. So under the selected fretting wear conditions, the tungsten carbide zirconia nanoceramic composites exhibits lower wear depth and higher wear resistance because of the hardness of the nanocomposite which is around 24 gigapascal.

(Refer Slide Time: 24:55)



The formation of mild abrasion scratches along with the finer sized debris indicates better wear resistance of the composite at lower load of 10 Newton, whereas at higher load of 5 Newton or more, tribochemical wear is the dominant mechanism of the material removal. The observation of the spalling induced by the cracking of this non-protective tribolayer and the formation of a sheet like debris also suggest severe at the higher load.

So this particular study indicates the wear behavior of the tungsten carbide zirconia nanoceramic composite depends on the load as well as the fretting duration. The mechanism of the material removal is changed from mild abrasion to tribochemical wear with change in the load from the 2 Newton to 10 Newton. Thank you.