Friction and Wear of Materials: Principles and Case Studies
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Lecture - 27
Overview: Nanoceramic Composites

Hello, welcome back to the NPTEL course and friction and wear of materials, case studies and principles. So today in this lecture, we will learn about a unique combination of properties that can be obtained in nanoceramics and nanoceramic composites. We will also focus on the processing techniques, particularly the spark plasma centring to develop such nanoceramic composites, and we will also see the overall view of this nanoceramic composites tribology.

Overall the tribological behavior of nanoceramic composites will also be understood. First nanostructured materials, by definition a material with the structural units having a size of scale of less than 100 nm in any dimension is called a nanostructured material.

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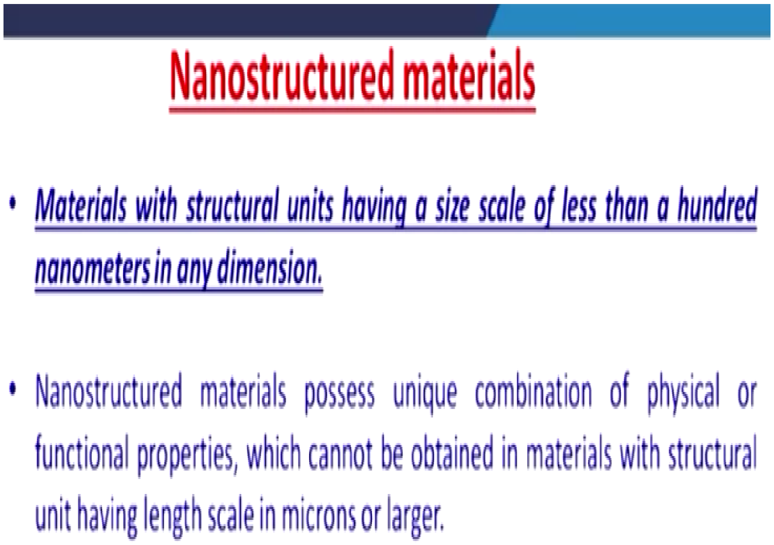

Nanostructured materials

- *Materials with structural units having a size scale of less than a hundred nanometers in any dimension.*
- Nanostructured materials possess unique combination of physical or functional properties, which cannot be obtained in materials with structural unit having length scale in microns or larger.

So nanostructured materials, they posses unique combination of physical or functional properties, which cannot be obtained in materials with structural units having scales in microns or larger, right. So nanostructured materials can be categorized based on their dimension.

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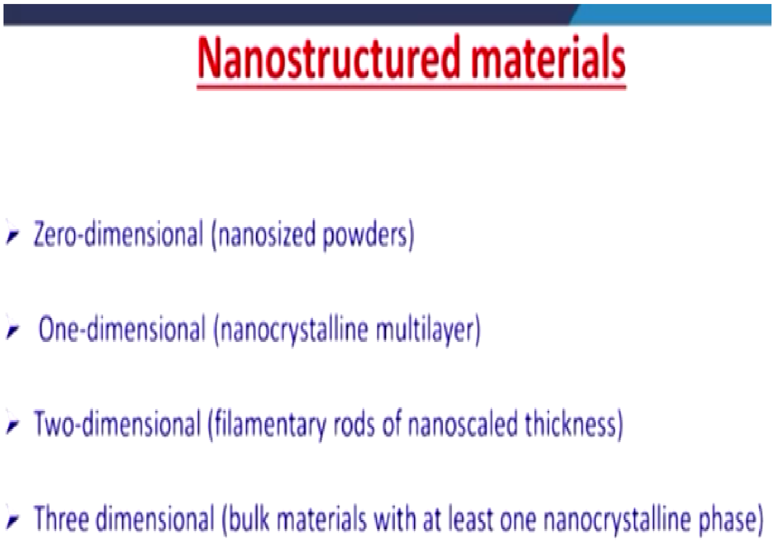

Nanostructured materials

- Zero-dimensional (nanosized powders)
- One-dimensional (nanocrystalline multilayer)
- Two-dimensional (filamentary rods of nanoscaled thickness)
- Three dimensional (bulk materials with at least one nanocrystalline phase)

Zero dimensional material, nanosized powders are 1 dimensional nanostructured materials. For example, nanocrystalline multilayers, 2 dimensional nanostructured material, filamentary rods of nanoscale thickness or 3 dimensional materials, bulk materials with at least 1 phase, which is in nanorange. So coming to the nanoceramic and nanoceramic composites, they have tremendous applications.

The intended applications of nanoceramics and nanoceramic composites include ceramic parts for the automotive engines, cutting tools, hit engine components are wear resistant parts, aerospace related industrial applications where all these advantages of having a superior combination of properties will be used. But the major challenge in nanoceramic development is the restriction of grain growth while achieving the full density.

For most of the mechanical applications or tribological applications you need a ceramic component with the full density, at the same time, you need to restrict to the grain growth to a nanorange, so that you get advantage of having a nanoceramic composites with respect to their property improvement.

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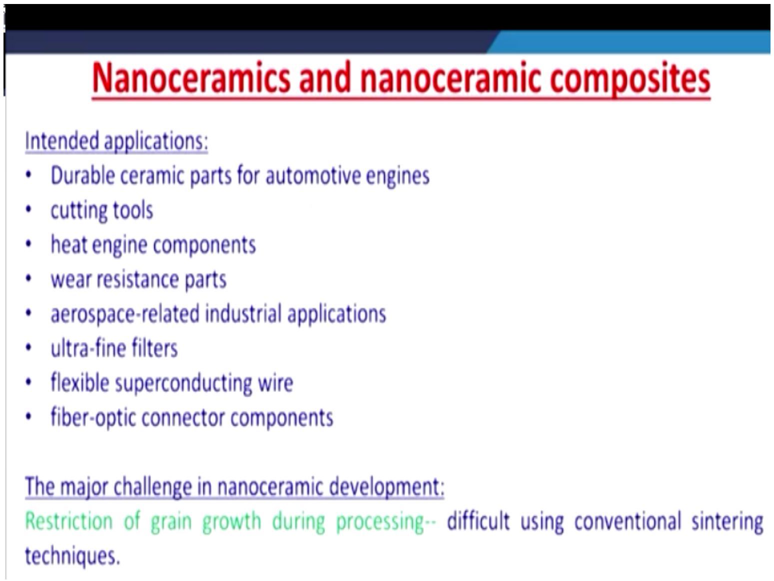

Nanoceramics and nanoceramic composites

Intended applications:

- Durable ceramic parts for automotive engines
- cutting tools
- heat engine components
- wear resistance parts
- aerospace-related industrial applications
- ultra-fine filters
- flexible superconducting wire
- fiber-optic connector components

The major challenge in nanoceramic development:
Restriction of grain growth during processing-- difficult using conventional sintering techniques.

But the restriction of grain growth during processing is very difficult using conventional sintering techniques.

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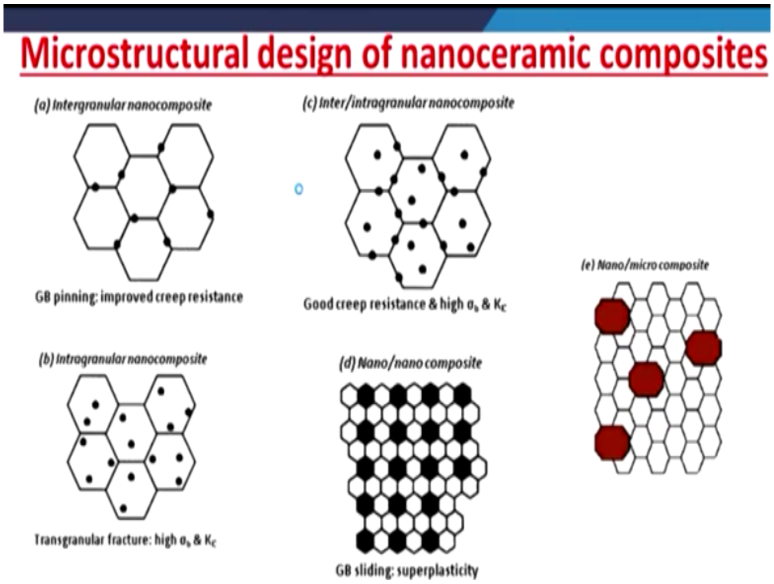

Microstructural design of nanoceramic composites

(a) Intergranular nanocomposite

GB pinning: improved creep resistance

(b) Intragranular nanocomposite

Transgranular fracture: high σ_s & K_C

(c) Inter/intragranular nanocomposite

Good creep resistance & high σ_s & K_C

(d) Nano/nano composite

GB sliding: superplasticity

(e) Nano/micro composite

We will also see advanced sintering techniques to develop such composites. First of all, the nanoceramic composites can be classified into 5 groups. One is intergranular nanocompodensisite, in which you a grain of a ceramic, which is not in nanosize, but you have reinforcement, which is in a nanosize and these reinforced phases are along the grain boundary. So you call this us intragranular nanocomposite.

Or you may also have a ceramic composite in which the grain of a ceramic, which is more than a nano dimension. The ceramic reinforcement, which is in nanosize range that can be inside the grains as well. So along the grain boundary as well as inside the grains, if then nano-reinforcement is available, so we call these as inter or intragranular nanocomposite or you may also have simply intragranular nanocomposite.

That means inside this ceramic grain you have a ceramic reinforcement, which is a nanophase. The nanophase is only inside the grain of this ceramic composite. So we call this as intragranular nanocomposite or you may also have a nanograin of nanomatrix with nano-reinforcement. So that is called nano-nanocomposite or you may also have a micro-nanosized matrix with micron sized reinforcement, you call it as nano-microcomposite.

That means you have overall 5 groups of nanoceramic composite.

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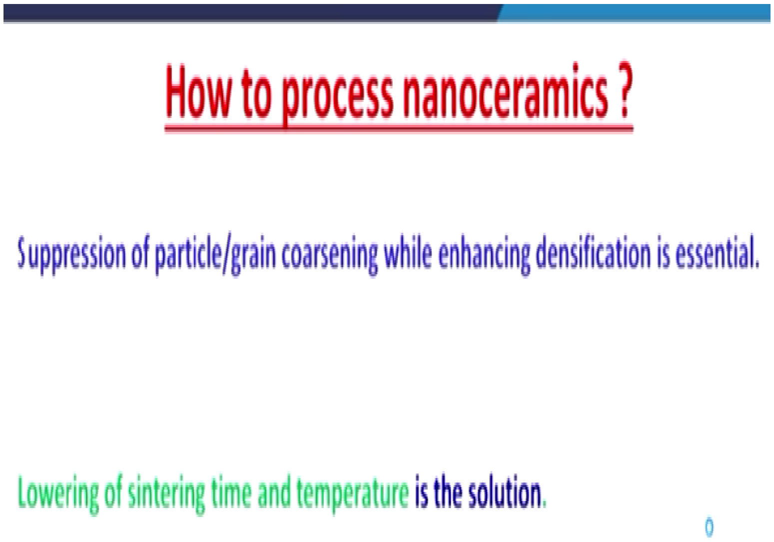

How to process nanoceramics ?

Suppression of particle/grain coarsening while enhancing densification is essential.

Lowering of sintering time and temperature is the solution.

Then first of all how to process such a nanoceramic.

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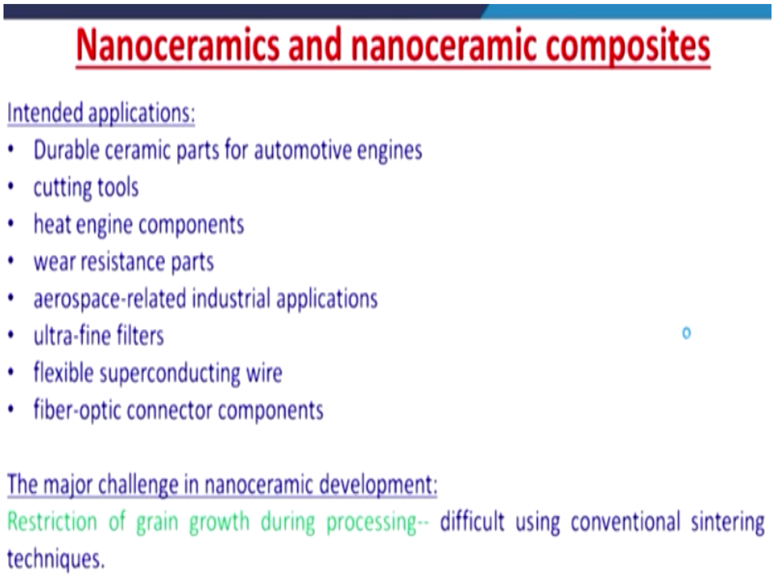

Nanoceramics and nanoceramic composites

Intended applications:

- Durable ceramic parts for automotive engines
- cutting tools
- heat engine components
- wear resistance parts
- aerospace-related industrial applications
- ultra-fine filters
- flexible superconducting wire
- fiber-optic connector components

The major challenge in nanoceramic development:

Restriction of grain growth during processing-- difficult using conventional sintering techniques.

As I told, it is very difficult to restrict the grain growth during processing using conventional sintering techniques. So a better understanding on the processing of ceramics is required to develop such a nanoceramic material. So the only solution to have such a suppression of the coarsening while enhancing the densification is by lowering the sintering time and temperature. So if you can lower the sintering time and temperature, we can restrict the coarsening, but you may have to maintain the densification.

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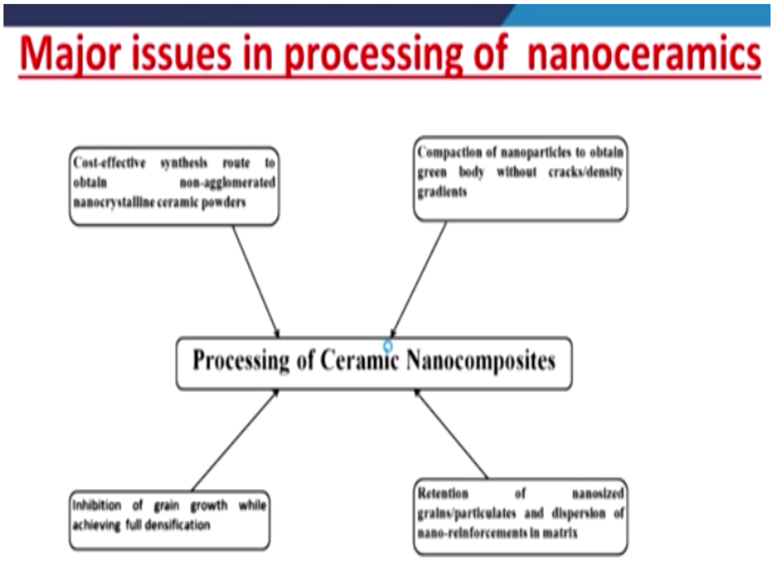

Major issues in processing of nanoceramics

Cost-effective synthesis route to obtain non-agglomerated nanocrystalline ceramic powders

Compaction of nanoparticles to obtain green body without cracks/density gradients

Processing of Ceramic Nanocomposites

Inhibition of grain growth while achieving full densification

Retention of nanosized grains/particulates and dispersion of nano-reinforcements in matrix

So in that sense you have the ceramic nanocomposites processing has major issues like inhibition of the grain growth while achieving full densification and retention of nanosized grains are particulates in the dispersion of nano-reinforcement in the matrix. So these are the major issues, but before that cost effective synthesis route to obtain a glomerate nanocrystalline ceramic powders.

In one of the previous classes, we learnt about mechanical synthesis for the ceramic powders. One of them is the ball milling. So you have to find a cost effective synthesis route to obtain a nano-agglomerated nanocrystalline ceramic powders. So usually when the size is reduced for the powders, they tend to agglomerate easily. So to obtain nano-agglomerated nanocrystalline ceramic powders, you have to find out one suitable synthesis route either chemical or mechanical synthesis, but it must be cost effective.

The other issue in the processing of nanoceramics is after having such nanoceramic powders, you have to compact it, right. So the compaction of nanoparticles to obtain grain body without having any density gradients or the cracks. This is a very challenging task, right. You have to find out such a compaction technique. So after that once the compaction is done, you have to do such a sintering.

While sintering inhibition of the grain growth while achieving full densification is the major challenge as told earlier and other important issue is the retention of such nanosized grains or nanosized particles and dispersion of nano-reinforcement in a matrix. So uniform reinforcement, uniform dispersion of this nano-reinforcement in matrix is very challenging. At the same time, retaining the nanosize while sintering is also a challenging task.

So you have mainly the major issues in processing such nanoceramics is to have a cost effective synthesis route to obtain non-agglomerated nanocrystalline ceramic powders or compaction of nanoparticles to obtain grain body without cracks or density gradient or inhibition of grain growth while achieving full densification, retention of nanosized grains or particulates and dispersion of nano-reinforcement in the matrix.

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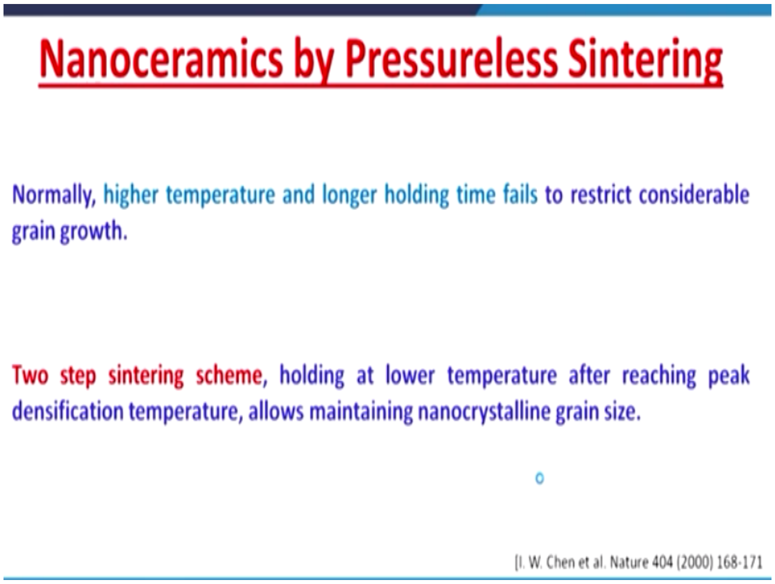

Nanoceramics by Pressureless Sintering

Normally, higher temperature and longer holding time fails to restrict considerable grain growth.

Two step sintering scheme, holding at lower temperature after reaching peak densification temperature, allows maintaining nanocrystalline grain size.

[I. W. Chen et al. Nature 404 (2000) 168-171

So coming to the processing techniques for such nanoceramics, first of all let us start with the very cost effective conventional sintering. We call it is a pressure less sintering. As we understood from the one of our previous classes, though sintering is the major step in developing a ceramic material and one of the cost effective sintering technique is the conventional sintering technique, which is a pressureless sintering technique.

In other techniques, we apply pressure, so those are called pressurized sintering techniques. A pressureless sintering technique, because of this cost effectiveness, is being used even in the industrial scale. But in this pressure less sintering normally higher temperatures are required and longer holding time are required to have such a dense ceramic body, but this holding at higher temperature for longer time lead to considerable grain growth.

So this is the major challenge in the pressureless sintering technique, but people have developed 1 very efficient scheme in the pressureless sintering technique to develop such a nanoceramic material is that one is the 2-step sintering scheme. So what do they do? In 2-step sintering scheme, first you hold it at lower temperature after reaching this peak densification temperature. So you have a peak densification. This is temperature and time.

So after achieving the peak densification temperature, where you expect a maximum densification is possible, so immediately after that you decrease the temperature, hold it at a lower temperature for longer time and before you cool it to a room temperature. So what you are actually doing? You are going to the maximum temperature, so that the diffusion is possible to a maximum extent.

So the necking happens to a maximum extent and you know the third phase of sintering as we understood from our previous classes, the third stage of sintering you have a considerable growth of the grains. So to minimize such growth of the grains immediately after achieving this third stage, that means after achieving this peak densification, you reduce the temperature and reduce it to lower temperature, so that the microstructural homogenity can be obtained.

So you have a 2-step sintering process, which is generally adopted in a conventional pressureless sintering technique to develop nanoceramic material.

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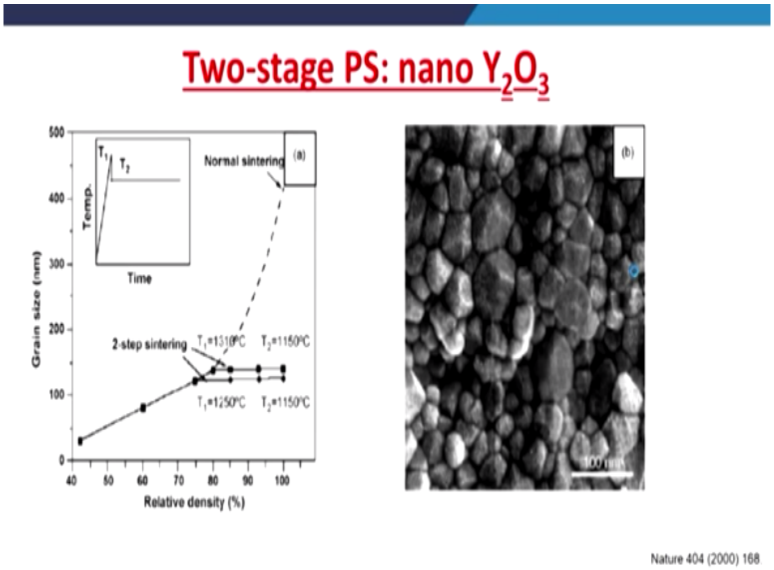

Two-stage PS: nano Y_2O_3

Nature 404 (2000) 168

So let us see a couple of examples of nanoceramic prepared by pressureless sintering technique by adopting such a 2-stage scheme. So this is a nano yttria ceramics. So you see the grain size versus the relative density. This is a normal sintering technique to achieve this kind of 99-100% relative density. You have to heat it to a very high temperature and hold it for a long time. So but this result into a larger grain size of more than 450 nm.

But the other technique is the 2-step sintering in which here you can see after this 1310 degree celsius, they decrease the temperature to 1150 and maintain it for longer time, so you get densification of 100%, whereas the grain size is restricted to around 150 nm. In other case also, there is a peak temperature followed by lower temperature holding. So you get a 2-step sintering resulting into a full densification, at the same time a grain size of around 120 nm.

So this is a typical microstructure of such nano yttria ceramic materials. You can see this is 100 to around 80 nm size grain in the sintered material, right.

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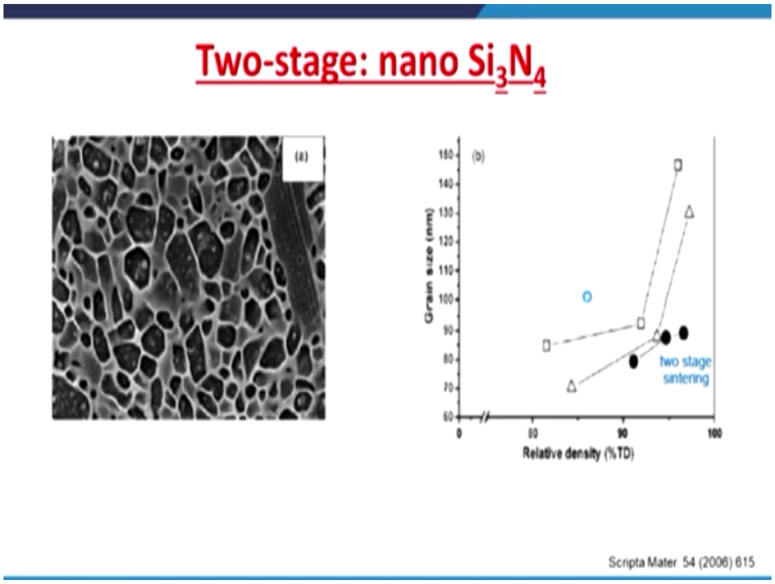

Two-stage: nano Si_3N_4

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This is one other example of nano silicon nitride ceramics, right. So here the investigators used silicon nitride with certain additive system and again maintained 2-stage sintering to achieve a nanosized grains in the silicon nitride ceramics. You can see a 2-staged sintering process. You have a density close to 97-98%, but the grain size is maintained around 80 nm, 85 nm. Whereas in normal conventional sintering you go to the similar densification, the grain size is more than 130, 145 nm.

So you get a densification to the maximum extent, but you can restrict the grain growth by adopting such a 2-stage sintering in a conventional pressureless sintering technique.

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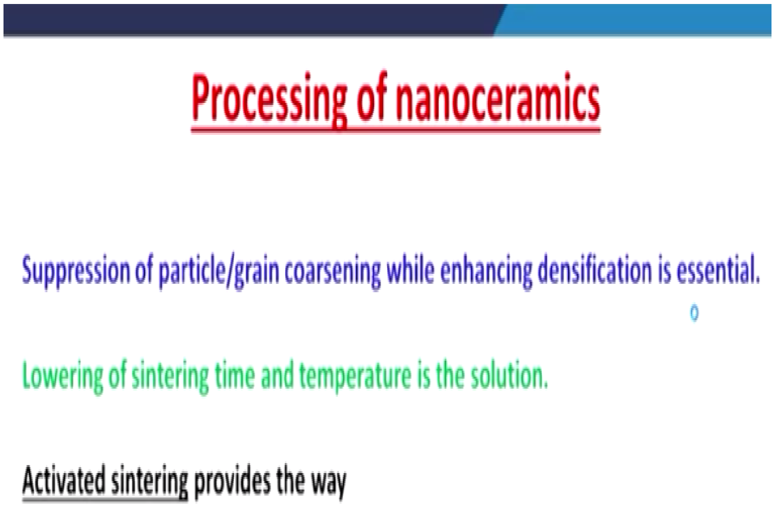

Processing of nanoceramics

Suppression of particle/grain coarsening while enhancing densification is essential.

Lowering of sintering time and temperature is the solution.

Activated sintering provides the way

But you know on the separation of this particle are grain coarsening, while enhancing the densification is a difficult task. So one other way to prepare such a nanoceramic material is by activated sintering. So let us see what is this activated sintering.

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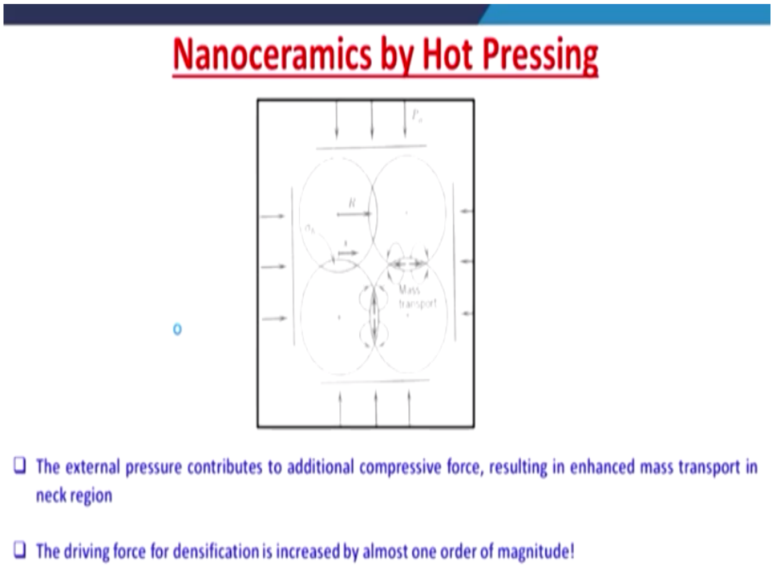

Nanoceramics by Hot Pressing

- The external pressure contributes to additional compressive force, resulting in enhanced mass transport in neck region
- The driving force for densification is increased by almost one order of magnitude!

So we understood from our previous class that one of the activated sintering technique is by hot pressing. So hot pressing what you do, you heat while pressing. You have a simultaneous application of pressing and then heating. So you see this is one schematic representation of pressing in all directions and then you can see the particles are forced to have contacts. So maximum number of contacts will be developed for the particles.

So at higher temperature, so because of the external pressure you have additional compressive force. So thus additional compressive force results into enhanced mass transport in the neck region. So you have lot of diffusion occurring that leads to easy sintering, right. So the driving force for such densification is increased by almost one order of magnitude when you compare with pressureless sintering. So this hot pressing is generally used for preparing a nanoceramic materials.

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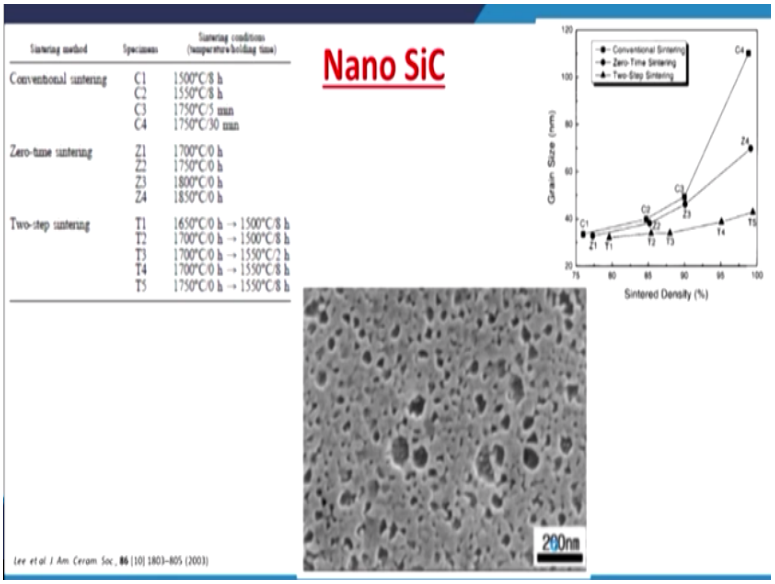

Nano SiC

Sintering method	Specimens	Sintering conditions (temperature/holding time)
Conventional sintering	C1	1500°C/8 h
	C2	1550°C/8 h
	C3	1750°C/5 min
	C4	1750°C/30 min
Zero-time sintering	Z1	1700°C/0 h
	Z2	1750°C/0 h
	Z3	1800°C/0 h
	Z4	1850°C/0 h
Two-step sintering	T1	1650°C/0 h → 1500°C/8 h
	T2	1700°C/0 h → 1500°C/8 h
	T3	1700°C/0 h → 1550°C/2 h
	T4	1700°C/0 h → 1550°C/8 h
	T5	1750°C/0 h → 1550°C/8 h

Lee et al. J Am. Ceram. Soc., **86** [10] 1803–805 (2003)

For example, is silicon carbide ceramics. So in this paper, there were several sintering methods used for this specimens with different temperatures and time, right. So this the sintered density to obtain around 97 or 98% density, the grain size is more than 150 nm, whereas at 2-step sintering, you can see the 2-step sintering, you can go almost like 99% density, but at the same time you can maintain the grain size of the silicon carbide to 40 nm.

When you do not have any sintering time, that means 0 sintering time that means after achieving peak temperature of 1700 or so, immediately they dropped the temperature, but again for achieving the densification of around 97-98% densification, the grain size is around 80 or 75 nm, right but the ceramic grain size is restricted to around 40 nm, if you do the 2-step sintering process, right. You can see all these grains is around 40 nm.

So this type of 2-step sintering is also used in hot pressing to obtain silicon carbide ceramics of around 40 nm grain size, right.

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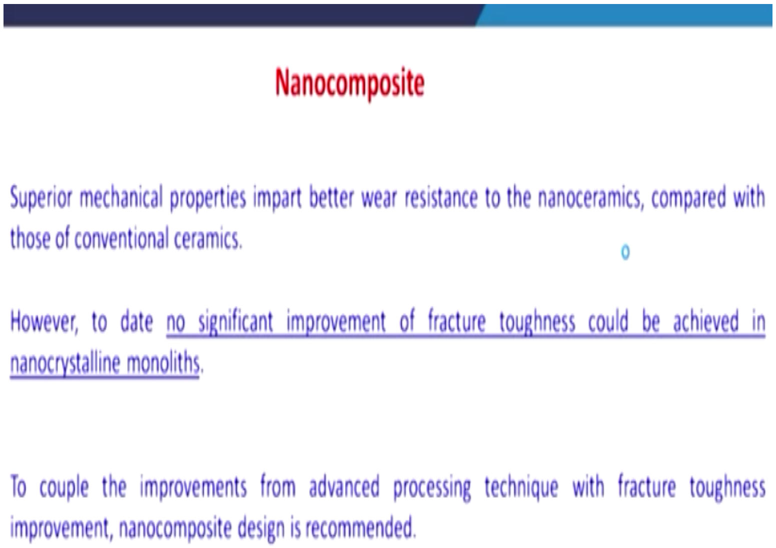

Nanocomposite

Superior mechanical properties impart better wear resistance to the nanoceramics, compared with those of conventional ceramics.

However, to date no significant improvement of fracture toughness could be achieved in nanocrystalline monoliths.

To couple the improvements from advanced processing technique with fracture toughness improvement, nanocomposite design is recommended.

We must understand the superior mechanical properties may in part improved wear resistance to the nanoceramics when you compare with conventional ceramic material. But due to significant improvement of fractured toughness cannot be achieved in monolithic nanocrystalline materials, a different approach called composite approach is suggested. So mainly to couple the improvements from advanced processing technique with fracture toughness improvement, a nanocomposite design is recommended.

And this is very famous paper, new design concept of structural ceramic nanocomposites by Koch Nihara. So he proposed initially that a nanocomposite design is much recommended to have an improvement in the properties particularly the combination of a fracture toughness and hardness. So if you have a such mechanical property improvement that includes a fracture toughness improvement also, then you may actually expect an improvement in the wear resistance. So let us see certain examples of these nanocomposites.

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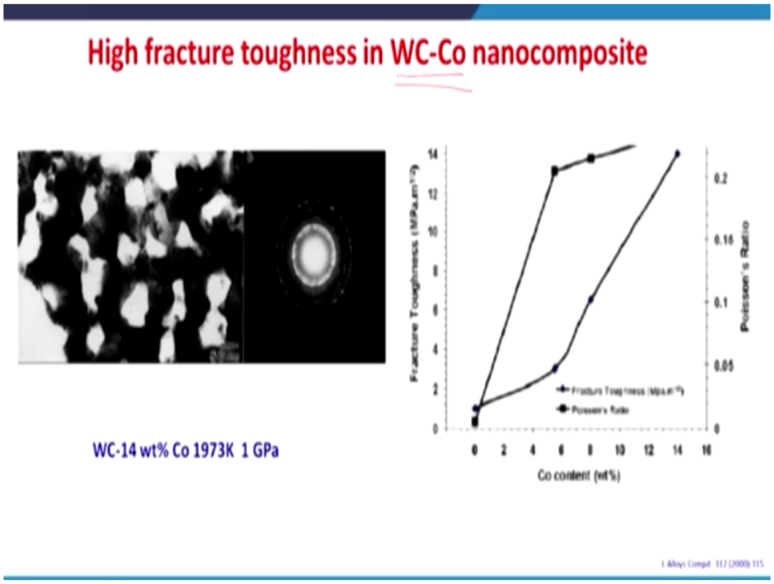

High fracture toughness in WC-Co nanocomposite

WC-14 wt% Co 1973K 1 GPa

J Alloys Compd 312 (2000) 315

Materials are called hard materials. These are called hard materials, particularly these are useful for ceramic cutting tool. These are particularly useful as a cutting tool. So these are called ceramides because a ceramic of tungsten carbide and cobalt which a metal. So cobalt is actually binding the tungsten carbide grains. So this particular example is shown for a tungsten carbide having 14% cobalt and hot pressed at again very high pressure 1 gigapascal at 1973 kelvin to result into a nanosized ceramic of tungsten carbide.

So you see as I told, you have a ceramic grain of this tungsten carbide and these tungsten carbide grains are attached through this cobalt binder phase, right. So the influence of the amount of cobalt is much useful. The influence of the amount of this cobalt, influence of cobalt content is very important on the mechanical properties improvement. For example, the fracture toughness can be improved by increasing the cobalt content. You see the fracture toughness.

See the fracture toughness increased it to a maximum value of around 14 mp/root meter with increase in the cobalt content in tungsten carbide cobalt nanocomposite, right. So cobalt is generally added to improve the fracture toughness. Tungsten carbide is responsible for the hardness and abrasion resistance, so you get a maximum wear resistance. So tungsten carbide cobalt nanocomposite with improved fracture toughness is much useful for cutting tool kind of applications, right.

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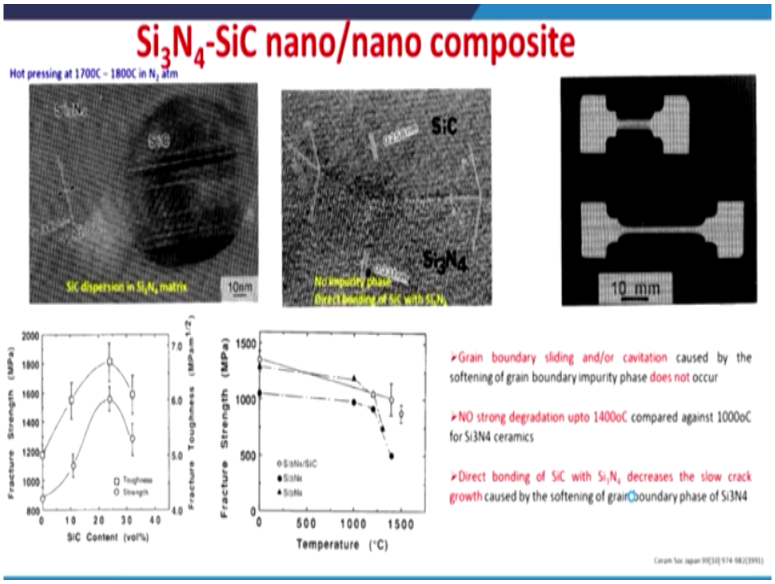

Si_3N_4-SiC nano/nano composite

Hot pressing at 1700C – 1800C in N_2 atm

- Grain boundary sliding and/or cavitation caused by the softening of grain boundary impurity phase does not occur
- NO strong degradation upto 1400oC compared against 1000oC for Si3N4 ceramics
- Direct bonding of SiC with Si_3N_4 decreases the slow crack growth caused by the softening of grain boundary phase of Si3N4

Ceram Soc Japan 99[10] 974-982(1991)

So as I told nanocomposites are used for mainly to have a combination of improved properties, 1 classical example is silicon nitride, silicon carbide nano-nanocomposite, in which the silicon nitride is a matrix, which is also in a nanoscale. The silicon carbide is a reinforcement, which is also in a nanoscale. So you can see these particles are subjected to hot pressing at 700-800 celsius in nitrogen atmosphere to develop such a nano-nanocomposite.

You can see the TM image of this composite. You see the silicon nitride grain and silicon carbide particle, right. So the silicon carbide is dispersed in the silicon nitride matrix. So even higher magnification image shows, you can see the silicon carbide this grain and silicon nitride grain, these are bonded almost without any impurity phase. So that means there is a direct bonding with silicon carbide and silicon nitride grains.

Actually such a direct bonding is responsible for improving the mechanical properties even at a higher temperature. If you see the fracture strength versus the temperature, you see the silicon nitride and silicon carbide composite, this is one. So you can retain almost higher strengths of around 1000 MPA even if you go to a temperature of around 1400 Celsius for the silicon nitride, silicon carbide nanocomposite.

So the fracture strength versus the silicon carbide content maximum fracture strength at room temperature like 1800 MPA is reported. A fracture strength of around 1500 MPA is reported if you have 25 volume % of silicon carbide and fracture toughness is maximum for this silicon nitride 25% silicon carbide composite and the maximum fracture toughness of around 6.6 MPA root meter is recorded for the silicon nitride, silicon carbide composite having a silicon carbide of around 25 volume%.

SO now how we do have an advantage of having such a nanocomposite with respect to performance. You can see the deformation. The deformation is much larger deformation is possible if you have such a nano-nanocomposite. Generally, the grain boundary sliding or cavitation are caused by the softening of the grain boundary impurity phases are responsible for the creep occurring at higher temperatures.

But because there is no impurity phase, the grain boundary sliding and/or the cavitation caused by that kind of grain boundary impurity phase softening is not occurring in these composites. So you have the strength retaining even at a higher temperature. So no strong degradation up to around 1400 Celsius compared to again it is 1000 Celsius for silicon nitride ceramic, right. So you can see after 1000 Celsius the silicon nitride strength is reduced.

Whereas silicon-nitride, silicon carbide nano-nanocomposite, it can maintain higher strengths even at around 1400 celsius. So you have an advantage of such around 400 degree celsius to maintain the higher strength levels, by adopting such nano-nano silicon nitride, silicon carbide composite approach, right.

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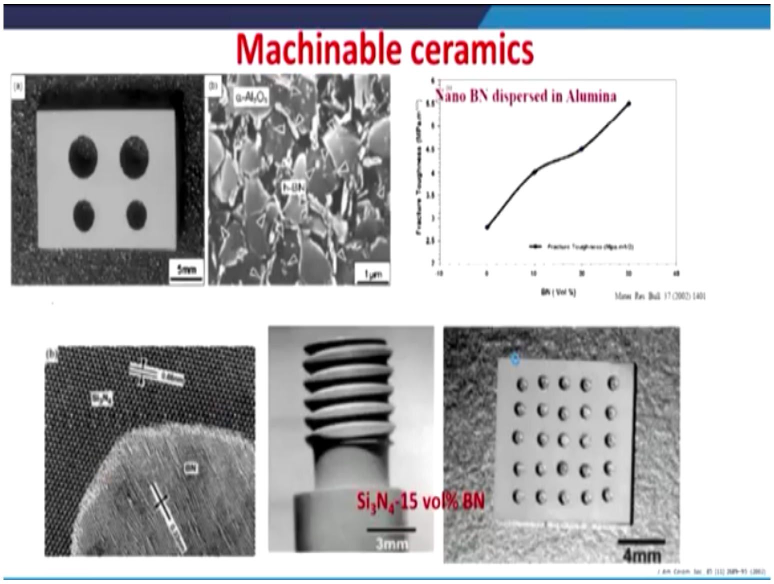

Machinable ceramics

Mater Res Bull 17 (2002) 1401

J Am Ceram Soc 85 [11] 2689-95 (2002)

So one other example to show the benefit of this nano-reinforcement is to develop machinable ceramics. This is very fancy thing and very interesting thing to understand; the ceramics are machinable here, right. Generally, as in when you start machine a ceramic, those ceramics will be failed in a catastrophic way because of the inherent brittleness, right. But you can develop a machinable ceramics with nanocomposite approach.

So this is one example of alpha aluminum oxide grains in which the boron nitride, which is the hexagonal boron nitride. This hexagonal boron nitride can be dispersed in aluminum oxide matrix and this nano hexagonal boron nitride can be useful in improving the fracture toughness, right. Because of the layered structure of this hexagonal boron nitride, it will be easy to machine such a composite having.

So the fracture toughness is improved with increasing such a hexagonal boron nitride content. One example, so you can see even drill this holes in aluminum oxide and boron nitride composite. One another example is silicon nitride with hexagonal boron nitride reinforcement. You can see the silicon nitride grain with boron nitride grain. Those are almost having very direct bonding with each other and you can even develops such a complex structures in this silicon nitride and boron nitride nanocomposite can even drill these ceramics.

So the machinable ceramics are possible when you go for a nanoceramic composite approach. So you have to find out a suitable processing conditions and you have to find out a suitable sintering technique to develop such a nanoceramic composite, so that you can have such an improvement in the performance. So let us understand this in more detail way. So only pressure application as we are doing in hot pressing does not always ensure grain growth restriction to nanocrystalline results.

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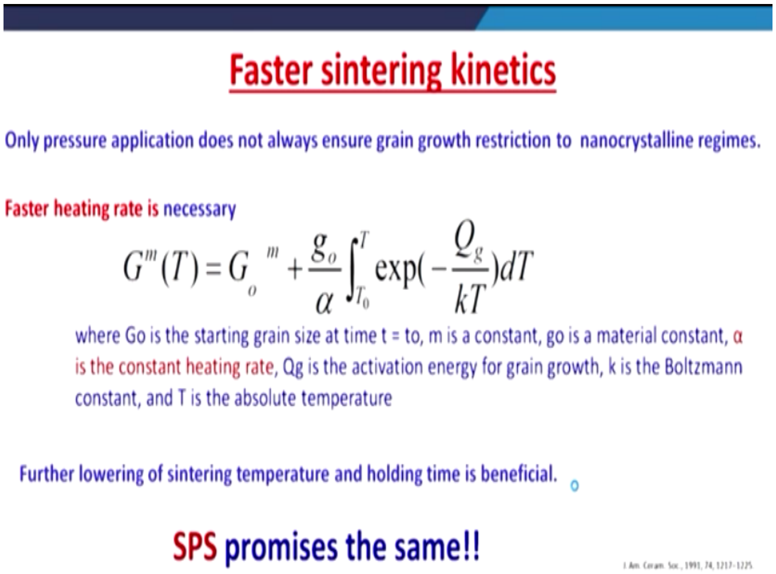

Faster sintering kinetics

Only pressure application does not always ensure grain growth restriction to nanocrystalline regimes.

Faster heating rate is necessary

$$G^{m}(T) = G_{o}^{\ m} + \frac{g_o}{\alpha}\int_{T_0}^{T} \exp(-\frac{Q_g}{kT})dT$$

where Go is the starting grain size at time t = to, m is a constant, go is a material constant, α is the constant heating rate, Qg is the activation energy for grain growth, k is the Boltzmann constant, and T is the absolute temperature

Further lowering of sintering temperature and holding time is beneficial.

SPS promises the same!!

J. Am. Ceram. Soc., 1991, 74, 1217-1225

Because you have an intrinsic pressure inside this small-sized particles, so it is very difficult to ensure this grain growth restriction for a nano powders at the same time maintaining the high densification by only pressing. So what you need to do, you have to have a faster heating rate. So if you see the grain size at a temperature of T, it is actually obtained by this equation where G0 is the starting grain size at initial time of 0 and M is a constant and G0 is a material constant.

Alpha is this constant heating rate and you can see this integral from T0 to T exponential of – QGP/K*T of dT. So QG is the activation energy for the grain growth, K is the Boltzmann constant and T is absolute temperature. So the striking point here is if you have a faster rates of heating, then you can maintain very minimal difference in this grain size that means the grain growth can be restricted if you go for a faster rates of heating, right.

So further lowering of sintering temperature and holding time is beneficial. So in this sense, the spark plasma sintering promises this. Actually, we have seen this spark plasma sintering in one of our previous classes only the principle. Let us understand this with more detailed way and with few examples of using this spark plasma sintering to develop such nanoceramic material. So let us see the spark plasma sintering.

As we understood it is pressing and heating that is similar to hot pressing, but heating is achieved in this spark plasma sintering by passing current through the electrically conducting pressure dyes or conducting powders. The consolidation happens in 2 stages.

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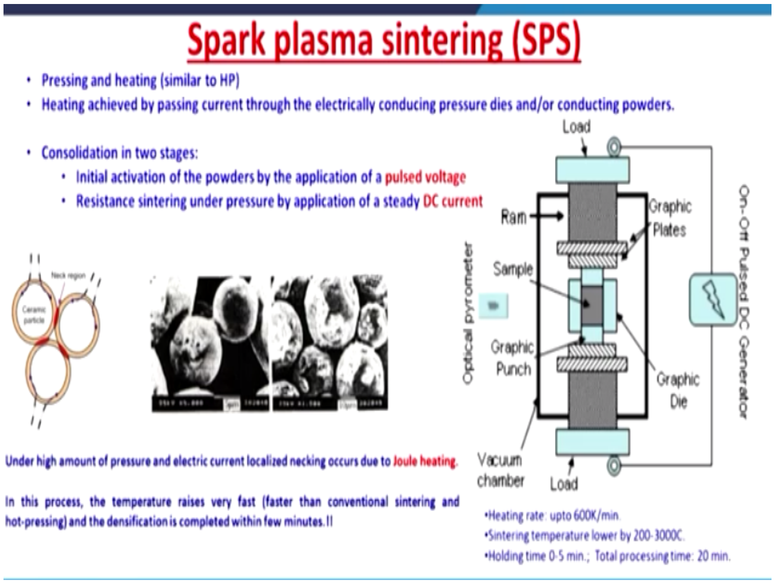

Spark plasma sintering (SPS)

- Pressing and heating (similar to HP)
- Heating achieved by passing current through the electrically conducing pressure dies and/or conducting powders.
- Consolidation in two stages:
  - Initial activation of the powders by the application of a pulsed voltage
  - Resistance sintering under pressure by application of a steady DC current

Under high amount of pressure and electric current localized necking occurs due to Joule heating.

In this process, the temperature raises very fast (faster than conventional sintering and hot-pressing) and the densification is completed within few minutes.!!

- Heating rate: upto 600K/min.
- Sintering temperature lower by 200-3000C.
- Holding time 0-5 min.; Total processing time: 20 min.

Initial activation of the powders by the application of a pulsed voltage followed by resistance sintering under pressure by application of a steady DC current. So in certain spark plasma sintering machines, these are done almost simultaneously. So if you see the mechanism in this spark plasma sintering under high amount of pressure and electrical current, there is a localized heating. This localized heating leads to necking.

And this localized heating is called joule heating, that joule heating leads to localized necking. So you can see the localized necking here. So in this process the temperature rises very fast and this temperature raise is at the contact where necking is happening. At that contact, there is a very high temperature that means you will have a high temperature at those places actually where you require, right.

So in this process the temperatures raises very fast and faster than the conventional sintering at even hot pressing and the densification is completed within few minutes. So as we understood in one of our previous classes, the total sintering cycle duration is of 20 minutes to 30 minutes' time in a spark plasma sintering whereas in hot pressing and conventional pressureless sintering, it is of few hours, right.

So in conventional pressureless sintering, it is of like 20-22 hours. So you see the 20 or 22 hours of sintering cycle is reduced to 20 minutes to 30 minutes of sintering cycle duration in spark plasma sintering. So you have such a benefit if you use this, by heating it at a very high rates of heating up to around 600 kelvin/minute. The sintering temperature can be lowered by 200 to 300 celsius. This is 300 celsius. The holding time is like 0 to 5 minute.

Total processing time is around 20 minutes. So if the powder is of conducting the current may pass through the powders as well. If it is not conducting, the current will pass through this dyes and punches and then there is an indirect heating of this powder. So this spark plasma sintering is useful to prepare such restricted grain growth, right.

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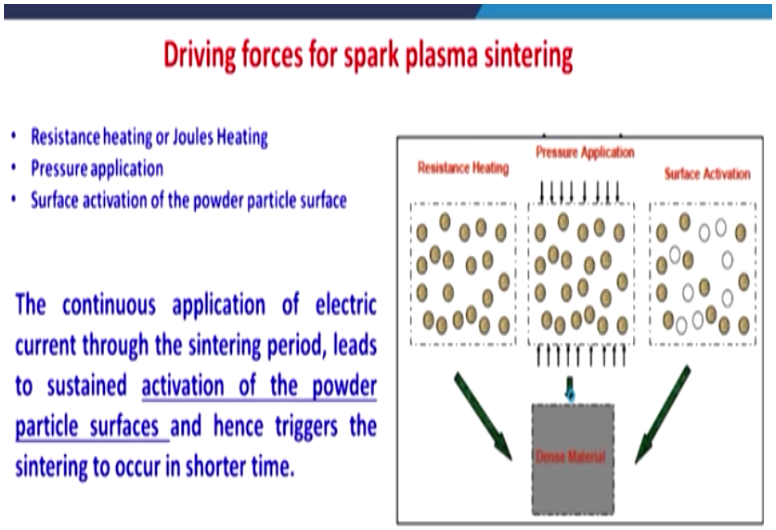

Driving forces for spark plasma sintering

- Resistance heating or Joules Heating
- Pressure application
- Surface activation of the powder particle surface

The continuous application of electric current through the sintering period, leads to sustained activation of the powder particle surfaces and hence triggers the sintering to occur in shorter time.

Driving forces for the spark plasma sintering are resistance heating or Joule's heating, pressure application and surface activation of the powder particle surface. So the powder particle surfaces are physically activated and then they lead to easy necking under this pressurized conditions and increased temperatures because of resistance heating. All 3 driving forces are responsible for easy sintering of this powder.

The continues application of electric current through the sintering period leads to sustained activation of this powder particle surfaces, therefore triggering the sintering to occur in a very shorted time.

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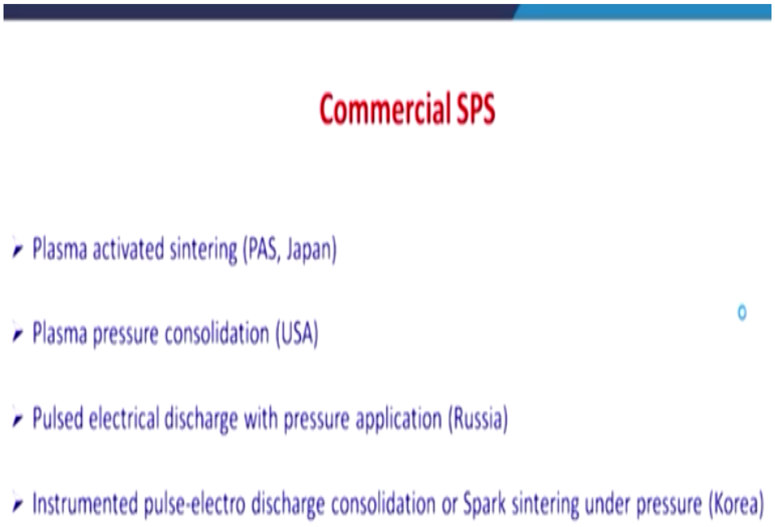

Commercial SPS

- Plasma activated sintering (PAS, Japan)
- Plasma pressure consolidation (USA)
- Pulsed electrical discharge with pressure application (Russia)
- Instrumented pulse-electro discharge consolidation or Spark sintering under pressure (Korea)

Commercially these spark plasma sintering machines are available with different names throughout the world. In Japan, these sintering machines or the sintering furnaces are called plasma activated sintering furnaces and the method is called plasma activated sintering. In USA, it is called plasma pressure consolidation, whereas in Russia, it is more popular with pulsed electrical discharge with pressure application whereas in Korea, it is more famous with instrumented pulse electrodischarge consolidation or spark sintering under pressure.

So these are different names for the commercially available SPS machines.

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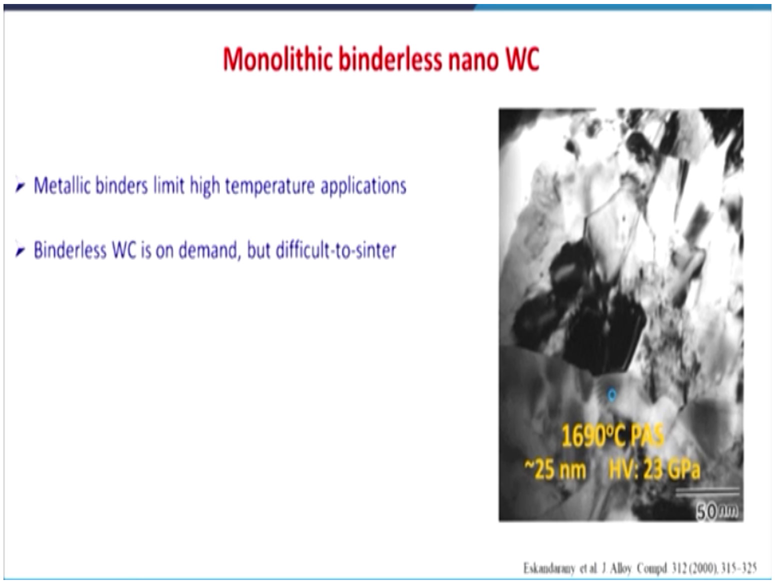

Monolithic binderless nano WC

- Metallic binders limit high temperature applications
- Binderless WC is on demand, but difficult-to-sinter

Eskandarany et al. J. Alloy. Compd. 312 (2000), 315-325

Let us just see few examples of nanoceramics prepared by such activated sintering technique. So this is a binder less nano tungsten carbide ceramic. As you know the tungsten carbide sintering is very much difficult because of its higher melting point and then very lesser diffusion coefficient because of the strong covalent bonding. So metallic binders limit high temperature application.

Generally, the tungsten carbide is sintered by adding certain metallic binders of cobalt--nickel-molybdenum, but this metallic binders limit high temperature applications. So the material will be degraded so because of its softening of this phase. So binder less tungsten carbide is on full demand, but you know the processing is difficult. As I told the sintering is very much difficult, but this spark plasma sintering at 1690 Celsius is sufficient to prepare a tungsten carbide binder less ceramic with a nanosize grain of around 25 nm and hardness of around 23 gigapascal.

So such a high hardness is possible because of this lesser size of these grains.

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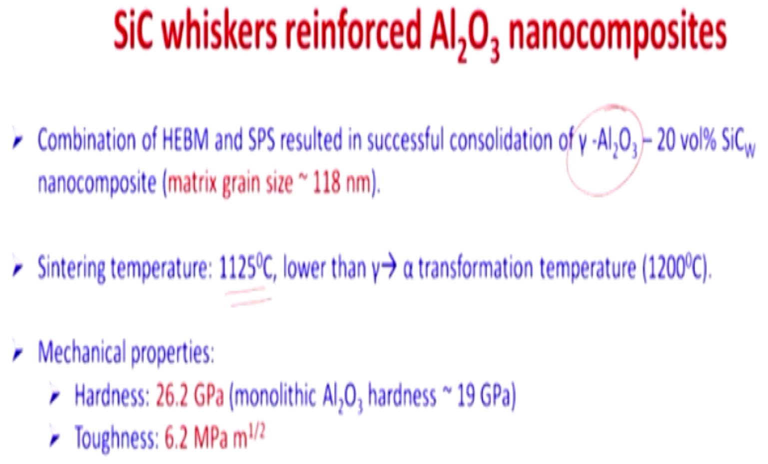

SiC whiskers reinforced Al_2O_3 nanocomposites

- Combination of HEBM and SPS resulted in successful consolidation of γ -Al_2O_3 – 20 vol% SiC_W nanocomposite (matrix grain size ~ 118 nm).
- Sintering temperature: 1125⁰C, lower than $\gamma \rightarrow \alpha$ transformation temperature (1200⁰C).
- Mechanical properties:
  - Hardness: 26.2 GPa (monolithic Al_2O_3 hardness ~ 19 GPa)
  - Toughness: 6.2 MPa $m^{1/2}$

Another example is aluminum oxide reinforced by silicon carbide whiskers. As you know silicon carbide whiskers are of very high strength, a combination of a high energy ball milling at spark plasma sintering resulted in successful consolidation of gamma aluminum oxide and silicon carbide whiskers nanocomposite, right. The composite having a matrix grain size of around 180 nm.

Remember the gamma phase is retained because the consolidation can be possible at a lower temperature of around 1125 celsius whereas there is the transformation to gamma to alpha transformation temperature is around 1200 celsius. So you can actually prepare a composite without having such a transformation from gamma to alpha. So such an advantage is possible only by this advanced sintering technique, spark plasma sintering technique.

So the mechanical properties of such a nanocomposite is also superior, the hardness of around 26 gigapascal. When you compare with monolithical alumina and the toughness can able be improved to 6MPA root meter. So a combination of hardness and toughness improvement can be possible by this nanocomposite approach.

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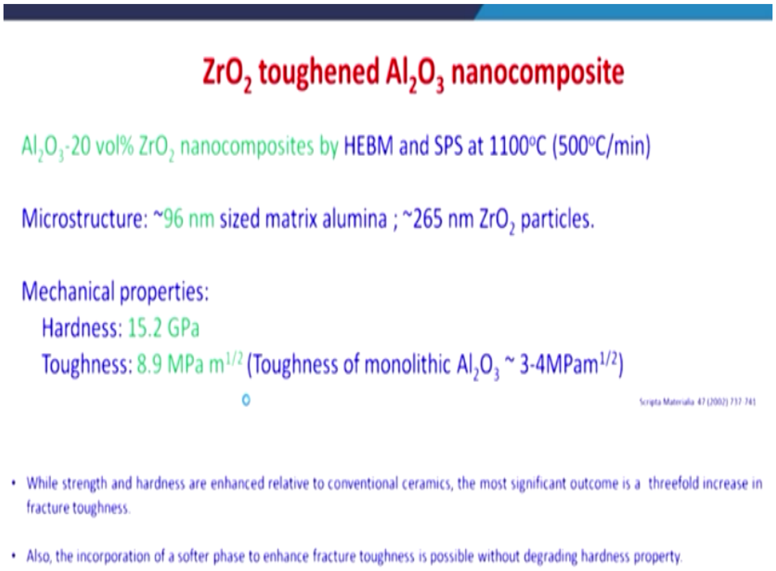

ZrO_2 toughened Al_2O_3 nanocomposite

Al_2O_3-20 vol% ZrO_2 nanocomposites by HEBM and SPS at 1100ºC (500ºC/min)

Microstructure: ~96 nm sized matrix alumina ; ~265 nm ZrO_2 particles.

Mechanical properties:
Hardness: 15.2 GPa
Toughness: 8.9 MPa $m^{1/2}$ (Toughness of monolithic Al_2O_3 ~ 3-4MPa$m^{1/2}$)

Scripta Materialia 47 (2002) 737-741

- While strength and hardness are enhanced relative to conventional ceramics, the most significant outcome is a threefold increase in fracture toughness.
- Also, the incorporation of a softer phase to enhance fracture toughness is possible without degrading hardness property.

Another very important example of nanocomposite is aluminum oxide, but this aluminum oxide is toughened by zirconium oxide. So aluminum oxide as you know the hardness is around 19 to 20 gigapascal, but the fracture toughness is very less among this ceramic materials, monolithic ceramic materials, tetragonal zirconium oxide exhibits a higher fracture toughness because of transformation toughening.

Because of this transformation induced toughening, zirconium oxide, monolithic ceramics have a fracture toughness of around 6-7 MPA root meter. So aluminum oxide ceramics if you reinforce with zirconium oxide, then you get improvement in the fracture toughness. So you see one example of high energy ball milling of these powders and then followed by spark plasma sintering at 1100 celsius at 500 celsius/minute heating rate to prepare aluminum oxide 20 volume % zirconium oxide nanocomposite.

A microstructural features revealed that 96 nm sized matrix alumina and zirconium oxide particle of around 265 nm. So it is a nanomicron composite. So in this example, aluminum oxide, which is toughen by the zirconium oxide particles. So the mechanical properties are hardness is around 15 gigapascal. As I told the aluminum oxide hardness is around 19 to 20 gigapascal. So it is reduced, but you can see the improvement in the fracture toughness.

The monolithic aluminum oxide the toughness is around 3-4 MPA root meter whereas aluminum oxide toughen by zirconium oxide exhibits a fracture toughness of around 9 MPA root meter. So you see almost like 3-9 MPA root meter. That means almost 3 times improvement in the fracture toughness, but a decrease in the hardness. So such a combination of an improvement in the fracture toughness with slight reduction in the hardness is possible by this nanocomposite approach.

So in general while strengthen hardness are enhanced relative to conventional ceramics, the most significant outcome is almost 3-fold improvement in the fracture toughness. So also the incorporation of a softer phase to enhance the fracture toughness is possible without degrading the hardness property. So the zirconium oxide hardness is lesser than the aluminum oxide hardness, but the fracture toughness is higher than the aluminum oxide fracture toughness.

So because of the toughening mechanisms involved in zirconium oxide, you have a benefit of almost 3-fold improvement in the fracture toughness for this aluminum oxide with zirconium oxide nancomposite.

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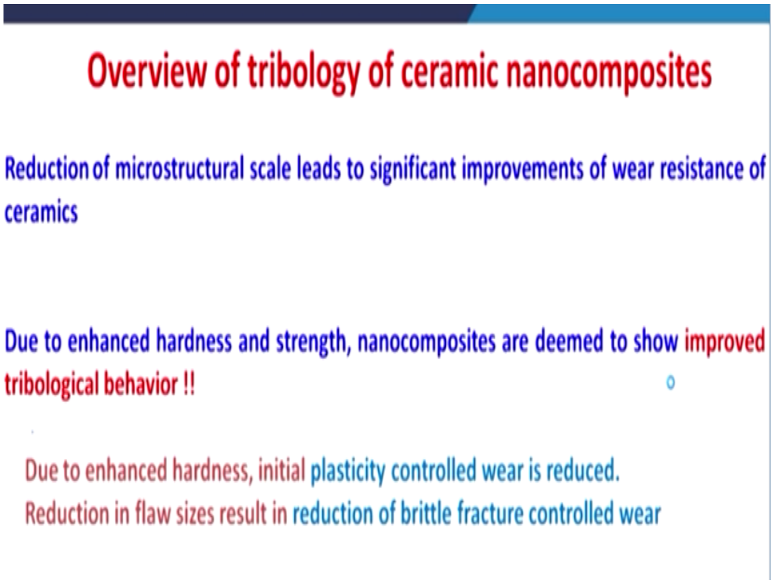

Overview of tribology of ceramic nanocomposites

Reduction of microstructural scale leads to significant improvements of wear resistance of ceramics

Due to enhanced hardness and strength, nanocomposites are deemed to show improved tribological behavior !!

Due to enhanced hardness, initial plasticity controlled wear is reduced.

Reduction in flaw sizes result in reduction of brittle fracture controlled wear

So all these improvement in the mechanical properties, for example hardness, toughness that we want to see the reflection in the tribological performance. In other classes, we will see several case studies, where such nanocomposite approach is beneficial in improving the tribological performance. Overall the reduction of the microstructural scale leads to significant improvement of the wear resistance of ceramic.

Due to enhanced hardness and strength, the nanocomposites are deemed to show improve tribological behavior. Mainly when you have only the wear occurring by abrasion that is by mechanical fracture method, the wear occurs mainly by plastically controlled wear and then brittle fracture. So in a nanoceramic composite due to enhanced hardness initial plasticity control wear is reduced and reduction in the flaw size result in reduction of brittle fracture controlled wear.

So both plasticity controlled wear and then brittle fracture controlled wear are reduced in a nanoceramic. So you can actually expect an improvement in the fracture toughness. In coming classes, we will see several example case studies where we can see the reflection of this mechanical property improvement on the tribological performance improvement.

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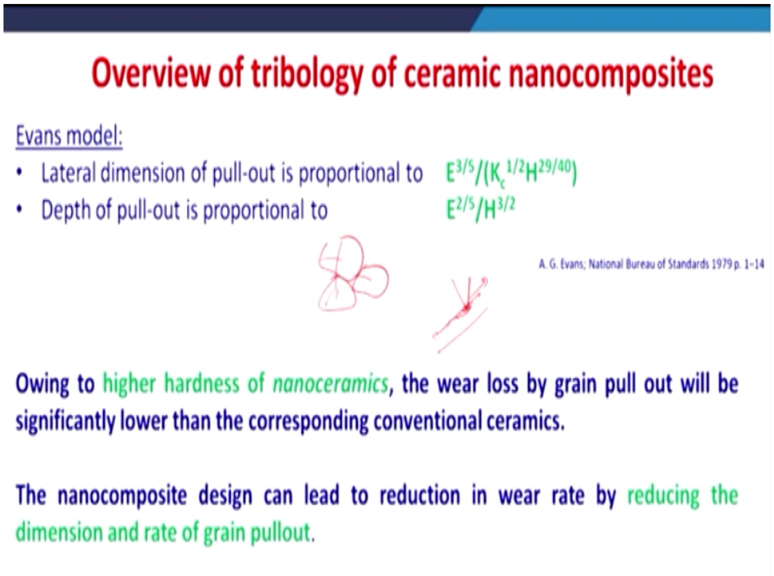

Overview of tribology of ceramic nanocomposites

Evans model:

- Lateral dimension of pull-out is proportional to $E^{3/5}/(K_c^{1/2}H^{29/40})$
- Depth of pull-out is proportional to $E^{2/5}/H^{3/2}$

A. G. Evans; National Bureau of Standards 1979 p. 1–14

Owing to higher hardness of *nanoceramics*, the wear loss by grain pull out will be significantly lower than the corresponding conventional ceramics.

The nanocomposite design can lead to reduction in wear rate by reducing the dimension and rate of grain pullout.

But let us see one very classical example of the tribology of ceramic nanocomposites. So it is a fracture induced wear that means we have certain grains and then fracture of these grains either by intragranular fracture or by transgranular fracture, the material is removed. So generally it happens in abrasion. When a harder material and sharper material is sliding over a brittle surface what happens? They generate certain lateral cracks.

The lateral cracks will lead to removal of the material. As the sliding is going on, there is a material removable by the lateral fracture. So the lateral fracture model that is proposed by Evans, lateral dimension of such pull out is proportional to this parameter, which is a combination of elastic modulus, fracture toughness and hardness and also the depth of pull out is proportional to this combination of elastic modulus and hardness.

So owing to higher hardness of nanoceramics, the wear loss by grain pull out will be significantly lower than the corresponding conventional ceramics. First, this hardness of this nanoparticle and nanocomposite design can lead to the reduction in the wear rate by reducing the dimension and the rate of grain pull out. So you have an advantage if you go for a nanocomposite.

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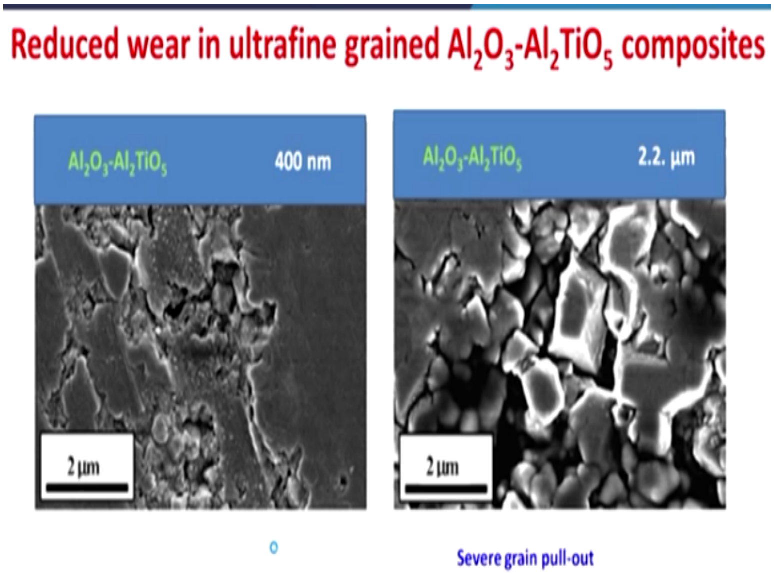

Reduced wear in ultrafine grained Al_2O_3-Al_2TiO_5 composites

Severe grain pull-out

This is one example to show such an advantage by going to a ultrafine grain ceramic composite, aluminum oxide, aluminum titanate with a finer grain size of around 400 nm and coarser grain size of around 2.2 micron meter. So you see there is a lot of pull out. So this pull out is because of the cracking along the boundary, grain boundary and then whole grain is actually removed, but you can see the severe grain pull out in a coarser grain sized composite.

Whereas a mild pull out in a ultrafine grain ceramic composite, so the wear resistance is actually improved by going to a ultrafine grain composite.

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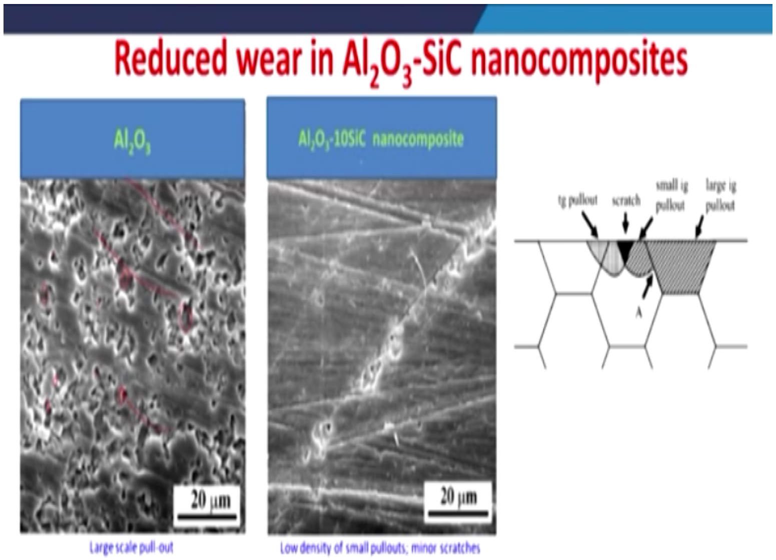

Reduced wear in Al_2O_3-SiC nanocomposites

Al_2O_3

Al_2O_3-10SiC nanocomposite

Large scale pull-out

Low density of small pullouts; minor scratches

So this example also show aluminum oxide silicon carbide nanocomposite is a monolithic aluminum oxide where you can see large scale pull out. There is a large cracking and then pull out. So there is too much of cracking and along with this abrasion. So abrasion leads to the cracking and then the material is pulled out. In case of aluminum oxide, 10% silicon carbide nanocomposite, you can see low density of very small pull outs and then minor scratches and very low density of this pull out.

That means the pull outs are reduced in a nanocomposite. So it can be modeled if you see the large pull out in a monolithic ceramic and nanocomposite, the pull out is actually reduced because of the presence of this silicon carbide nanoparticle. So as it was shown, the lateral dimension of pull out as well as the depth of pull out, both are reduced and then that leads to improvement in the wear resistance.

So you can see the material is damaged in a lesser extent in a nanocomposite compared to a monolithic ceramic.

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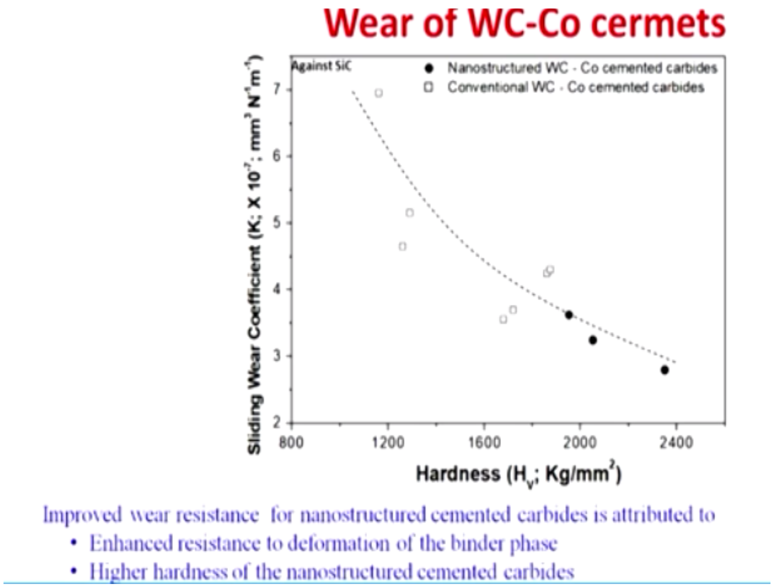

Wear of WC-Co cermets

Improved wear resistance for nanostructured cemented carbides is attributed to

- Enhanced resistance to deformation of the binder phase
- Higher hardness of the nanostructured cemented carbides

Finally, one example of the wear behavior of tungsten carbide, cobalt ceramides, which is a sliding wear rate, right MMQ/newton meter. This is hardness. You can see these are the conventional ceramide materials, the tungsten carbide cobalt ceramides material, these are all so called cemented carbides or hard materials. You can see these are nanostructured tungsten carbide cobalt cemented carbides, see against to silicon carbide sliding.

So as the hardness is increased in this material, the sliding wear rate is actually decreased, but you can see further decrease in the wear rate in the nanostructured tungsten carbide cobalt cemented carbides. So the improved wear resistance for the nanostructured cemented carbides is mainly attributed to enhance resistance to the deformation of binder phase and higher hardness of the nanostructured cemented carbide.

So in all these cemented carbides, as it was told earlier, these ceramic grains of the tungsten carbide are attached by this cobalt phase. This is cobalt phase. So while sliding against this harder silicon carbide what happens the material which is softer in nature that is less harder in nature is easily smeared out or deformed or removed. Once the material of the softer phase that is the binder phase is removed, then there happens a fracture of this ceramic grains.

Those are tungsten carbide grains. So now when you have a nanostructured tungsten carbide cobalt cemented carbide, the enhanced resistance to deformation is possible. So deformation of the binder phase is also restricted and higher hardness of the nanostructured materials. You can see the hardness is higher than the conventional ones. Conventional ones having around 1800 number or kg/mm square whereas hardness is much more in the nanostructured materials.

So the higher hardness of the nanostructured cemented carbides. When it is subjected to, when the contact is happening because of the higher hardness of this nanosized grains of the tungsten carbide, the resistance against the wear is also improved. So improved wear resistance mainly attributed to enhance resistance deformation and higher hardness of the nanostructured cemented carbides.

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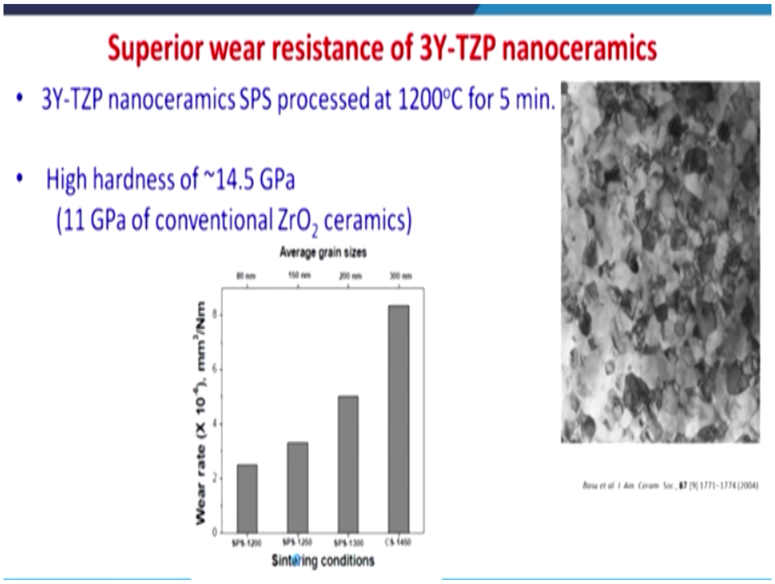

Superior wear resistance of 3Y-TZP nanoceramics

- 3Y-TZP nanoceramics SPS processed at 1200°C for 5 min.
- High hardness of ~14.5 GPa
  (11 GPa of conventional ZrO_2 ceramics)

Basu et al. J. Am. Ceram. Soc., 87 [9] 1771–1774 (2004)

So finally one example to show the wear resistance of this tetragonal zirconia polycrystalline material, this zirconia is stabilized by 3% yttria, right and this was processed by spark plasma sintering at 1200 Celsius for 5 minutes and you can see all this grain size is around 80-100 nm. A higher hardness of around 14.5 gigapascal is achieved for the nanoceramics and monolithic ceramic of zirconia ceramics generally has hardness of around 11 GPA.

Now you see this spark plasma sintering temperatures are varied and then you can see the grain size is reduced. The grain size is reduced when the temperature is less and the conventional sintering of hot pressing at 1450 Celsius that resulted into 300 nm. So comparing the wear rates of these conventional hot pressing and the spark plasma sintered materials, as the grain size is decreased, the wear rate is also decreased.

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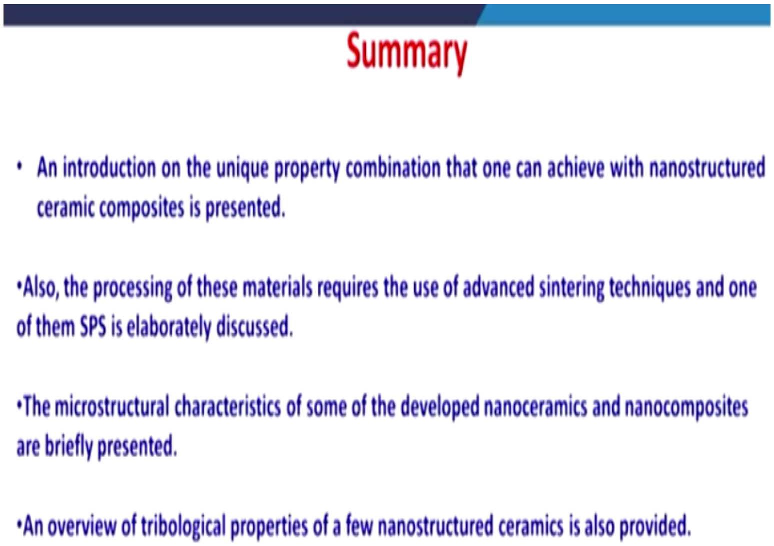

Summary

- An introduction on the unique property combination that one can achieve with nanostructured ceramic composites is presented.
- Also, the processing of these materials requires the use of advanced sintering techniques and one of them SPS is elaborately discussed.
- The microstructural characteristics of some of the developed nanoceramics and nanocomposites are briefly presented.
- An overview of tribological properties of a few nanostructured ceramics is also provided.

So we will also see several other case studies where we will also see several other case studies in coming classes for the reflection of the mechanical properties improvement in a nanocomposite materials on the tribological performance improvement. So summarizing today’s class, so an introduction on the unique property combination, that one can achieve with nanostructured ceramic composite is presented and then the processing of these materials required the use of advanced sintering techniques.

We have gone through elaborately one spark plasma sintering technique and hot processing, also we learnt that the processing of this material requires the use of advanced sintering techniques and one of the spark plasma sintering is elaborately discussed. The microstructural characteristics of some of the developed nanoceramics and nanocomposites are briefly presented. In addition to that an overall of tribological property of a few nanostructured ceramics is also provided.

So in the coming class, we will see few example case studies where we can see the reflection of the mechanical property improvement on the tribological performance improvement for important nanostructured ceramics and ceramic composites.