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 – 36
Erosive Wear of Ultra-High Temperature ZrB2-based Ceramic Composites

So, welcome back to these course of friction and wear of materials principles and case studies, so in the case studies part now, today we will see the erosion wear of ultrahigh temperature ZrB2 based ceramic composites and their respect results, so the outline of these present lecture is first I will introduce this ZrB2 SiC is a ceramic composites, ultrahigh temperature ceramic and then motivation as well as objectives of the present study and then experimental approach used for making this material as well as the erosion wear studying.

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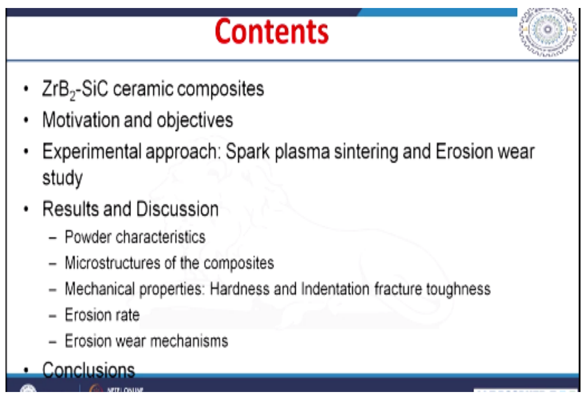

And then mainly we will discuss the powder characteristics, the microstructures of the sintered composites, mechanical properties, erosion rate and the dominant mechanisms of material removal, so let us start with the ZrB2 SiC composites, these are ultrahigh temperature ceramic composites particularly the ZrB2 which is zirconium di boride is a material with very high melting point.

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You can see this is more than 3200 Celsius and which has a high thermal conductivity and it is very hard material, it is 22 to 23 gigapascal and a stiffer material, Young's modulus is around 500 gigapascal with a good electrical conductivity and moderate density and it has excellent chemical and physical stability in various atmospheres, so these ceramics components, the components made by these ZrB2 are preferred for the nose of this space shuttle.

So, particularly when the space shuttle renters into the earth's atmosphere because of the additional gravitational pull, the friction induced heat will be few thousands of Celsius, so it is actually estimated by simulation studies at least 1300 to 1500 Celsius temperature is generated at the; this nose edges, so these ceramics are generally preferred for the components in the space shuttle, particularly when there is a chance for the high temperature generation.

And it has good mechanical properties as well and ZrB2 ceramics when reinforced with silicon carbide, there is an improved oxidation resistance and also the strength also improves so, typically from 300 to 500 mpa to 800 to 1000 mpa with the addition of silicon carbide in a ZrB2 matrix.

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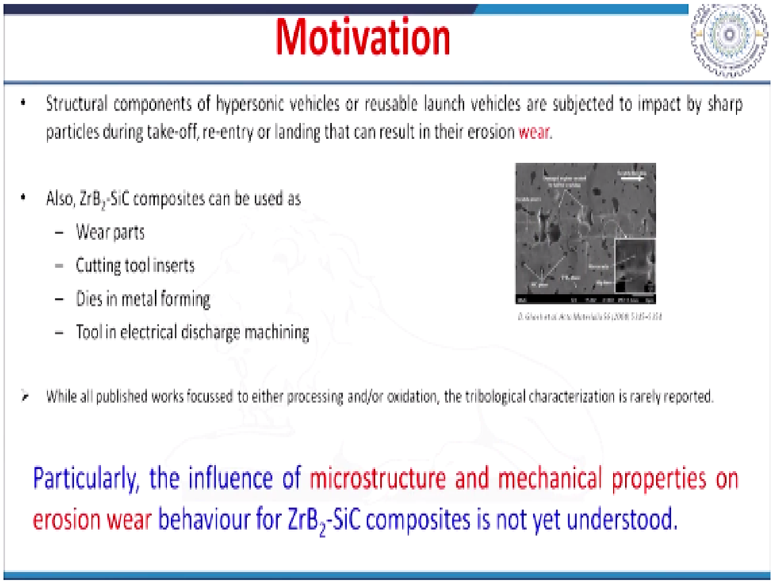

So, structural components of hypersonic vehicles or reusable launch vehicles are subjected to impact by sharp particles during their take-off or re-entry are landing, so that can eventually result into the erosion wear, also these composites can be used as wear parts or cutting tool inserts, dyes in metal forming or tools in electrical discharge machining, so that indicates actually these composites are to be understood for their tribological behaviour.

While all published works on these composites are focused mainly on the processing or by on the oxidation resistance of this material but tribological characterisation is very, very rarely reported so, with this motivation we try to understand the wear behaviour in erosion conditions with the change in the silicon carbide composites, so the particularly the influence of the microstructure by change in the composition and the mechanical properties again by change in composition on the erosion wear behaviour of this composites is of our interest.

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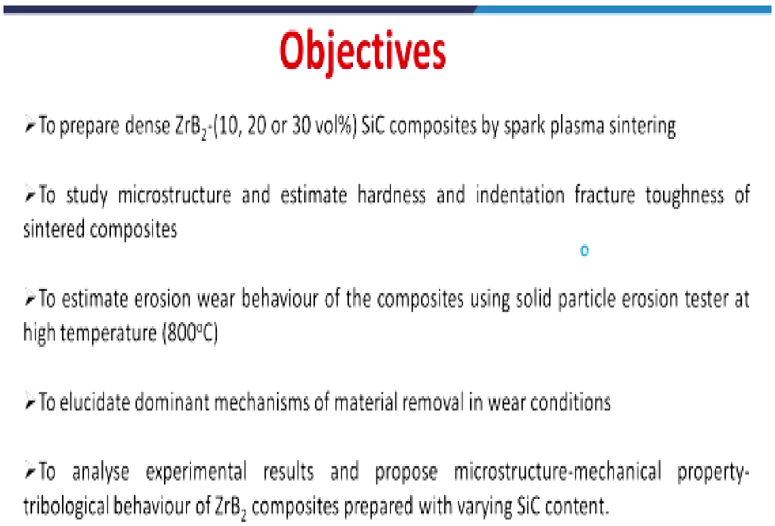

So, this is one study which shows some scratch resistance for these composites but no other important studies were done on their wear properties. So, objectives of the present study are to prepare the dense composites of ZrB2 with 10, 20 or 30 volume percent silicon carbide by spark plasma sintering, to study the microstructure and estimate the hardness and indentation fracture toughness of the sintered composites to estimate the erosion wear behaviour of the composites by particle erosion at high temperatures and to elucidate the dominant mechanisms of material removal in those selected erosion wear conditions.

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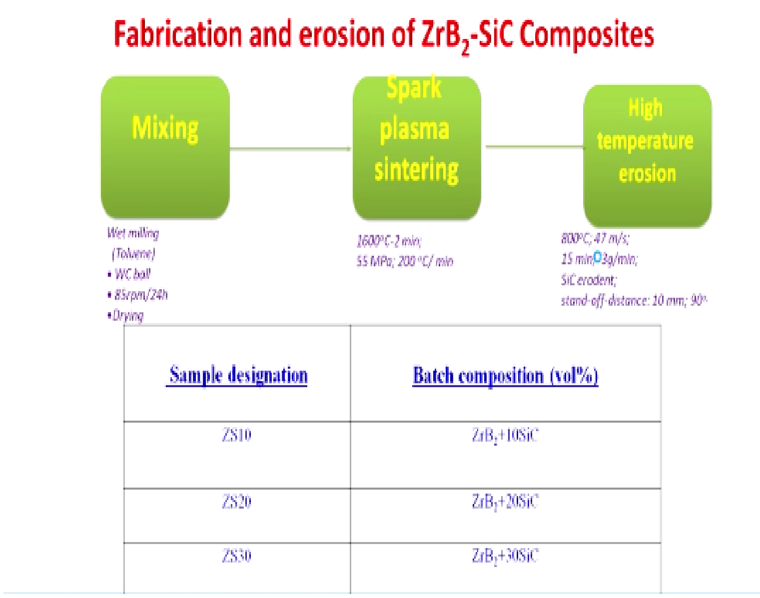

Sample designation	Batch composition (vol%)
ZS10	ZrB_2+10SiC
ZS20	ZrB_2+20SiC
ZS30	ZrB_2+30SiC

So, first the fabrication of this composites was done by spark plasma sintering, the powders of this zirconium di boride and the silicon carbide, they were mixed in ball mill with toluene and tungsten carbide balls and then spark plasma sintered and followed by the erosion.

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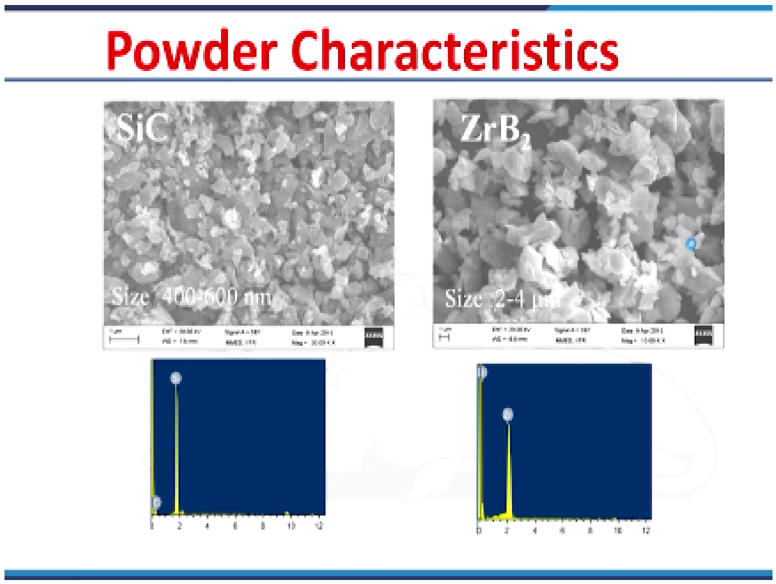

The initial powder characteristics show that the silicon carbide is around 400 to 600 nanometers in average size, whereas ZrB2 is in 2 to 4 micron meters average size.

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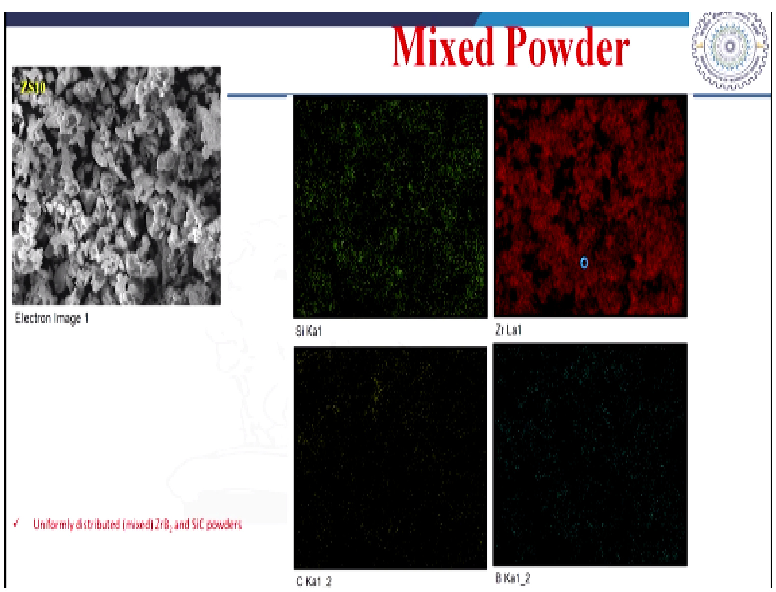

And their chemical characteristics also show there is no much impurity, so after mixing these ZrB2 SiC composite, they show uniform distribution.

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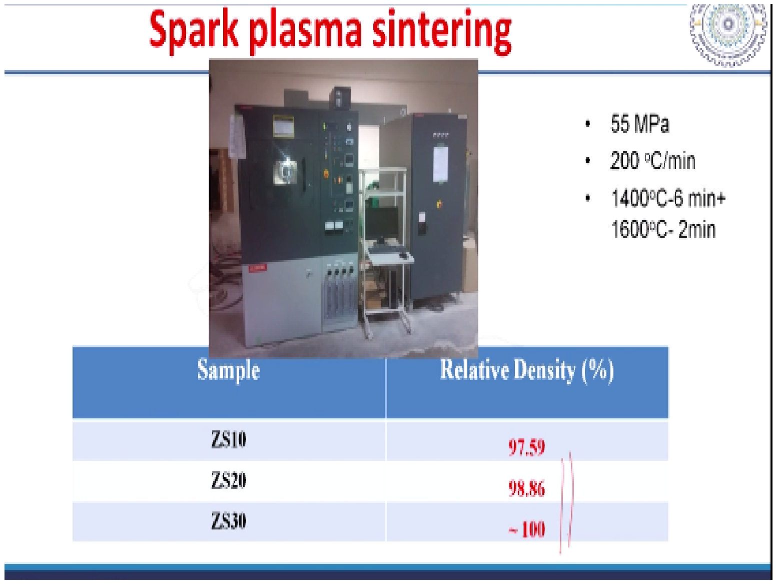

So, with this uniformly distributed particles, we went to spark plasma sintering, spark plasma sintering was done at 55 megapascals with a 200 degree Celsius per minute heating rate with a 2 stages sintering procedure 14000 Celsius for 6 minutes followed by 1600 for 2 minutes and these sintering cycle was selected from the previous reports, so all these composites with 10, 20 and 30% silicon carbide containing ZrB2 composites.

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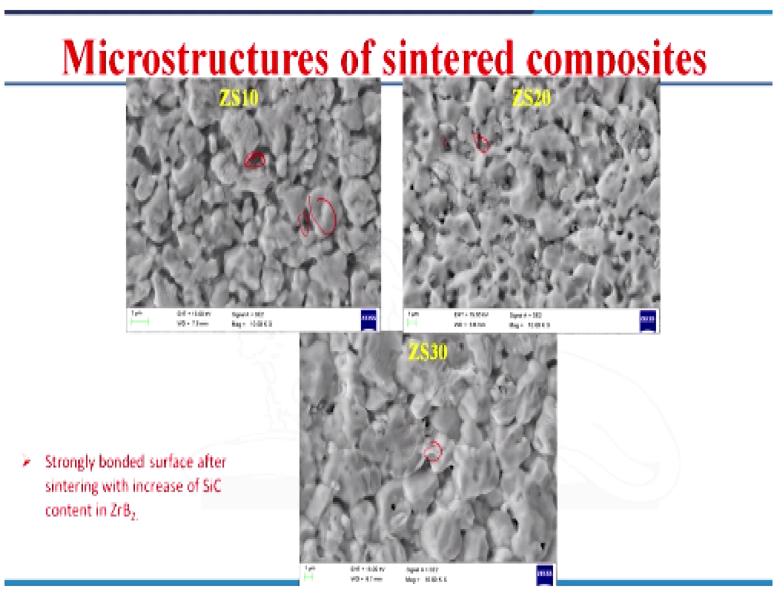

After sintering, they showed a decent relative density 98%, the microstructure of the sintered composites, they showed the ZrB2 and then this is silicon carbide, right so the silicon carbide, so with increase in the silicon carbide content, the bonding between the ZrB2 and the silicon carbide also seems to be increased, right so you can see very strong bonding of these with the increase in the silicon carbide content.

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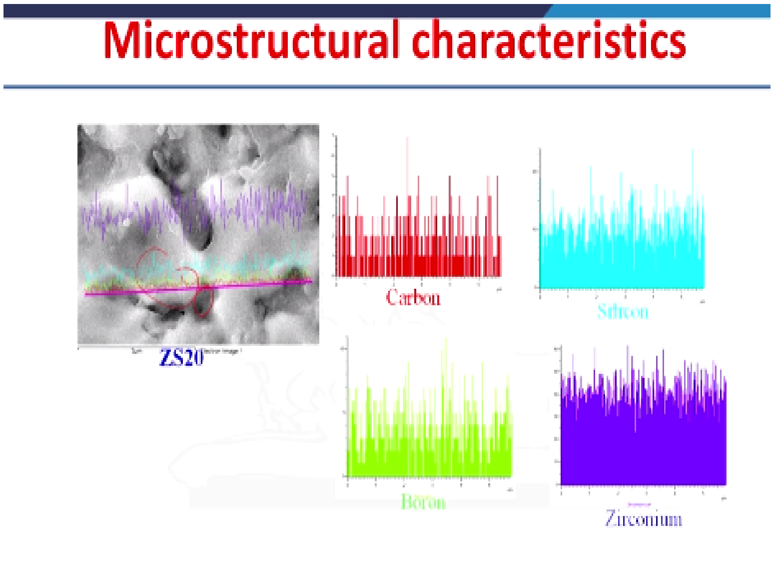

Also, the line analysis show there is a ZrB2 and then the silicon carbide, so you can see the ZrB2 and silicon carbide in the microstructure.

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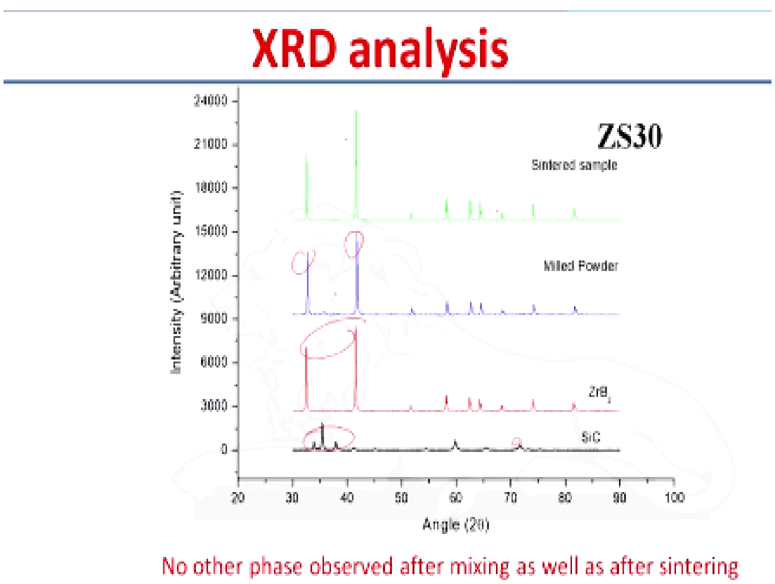

The x-ray diffraction analysis of the sintered composite show no other face after mixing as well as after sintering, so these are the initial powder XRD patterns of silicon carbide and ZrB2 where same ZrB2 SiC were found after milling, so you can see that ZrB2 and SiC so, no much change even after the sintering.

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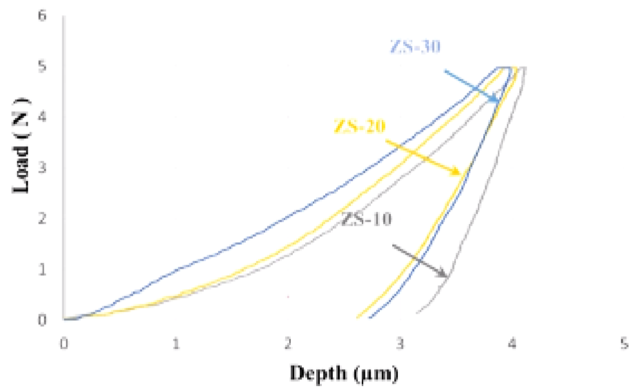
Mechanical properties



So that means our sintering procedure was efficient to sinter these composites without producing any other phases and the mechanical properties were studied, so this micro hardness measured using a instrumented hardness measurement tester, the depth decreases with the increase in the silicon carbide content.

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Mechanical Properties

Sample	Micro hardness (GPa)	Elastic Modulus (GPa)	Fracture toughness ($MPa.m^{1/2}$)
ZS10	18.13	280	4.2
ZS20	22.28	300	4.4
ZS30	23.53	398	5.3

So, the micro hardness also show there is an increase with the silicon carbide content from 18 to 23 gigapascal hardness for the ceramics with 10% silicon carbide to 30% silicon, the elastic modulus is also increased from 280 to 398 gigapascal and fracture toughness also increased from 4.2 to 5.3 mpa root meter.

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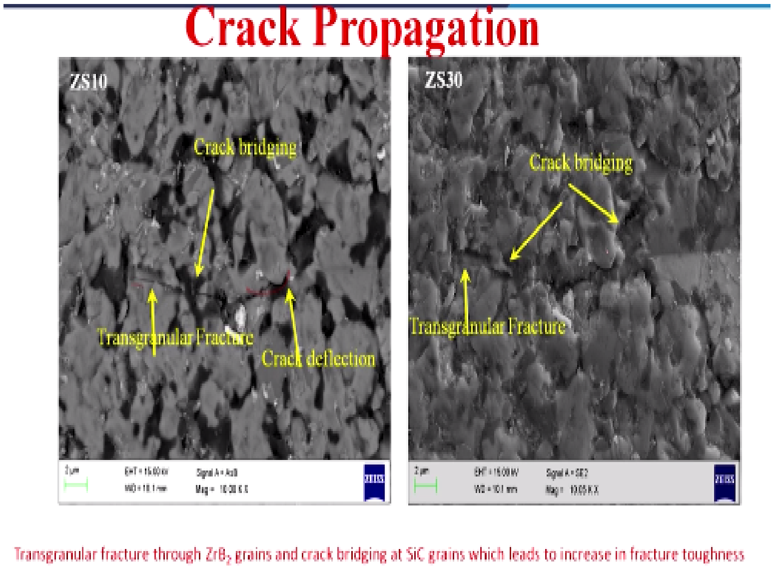

So, the fracture toughness improvement can also be understood by their increased crack bridging instances, so that the trans granular fracture, the crack propagates through the grain and then crack is deflected or bridged by these silicon carbide particles, so we get an improvement in the fracture toughness.

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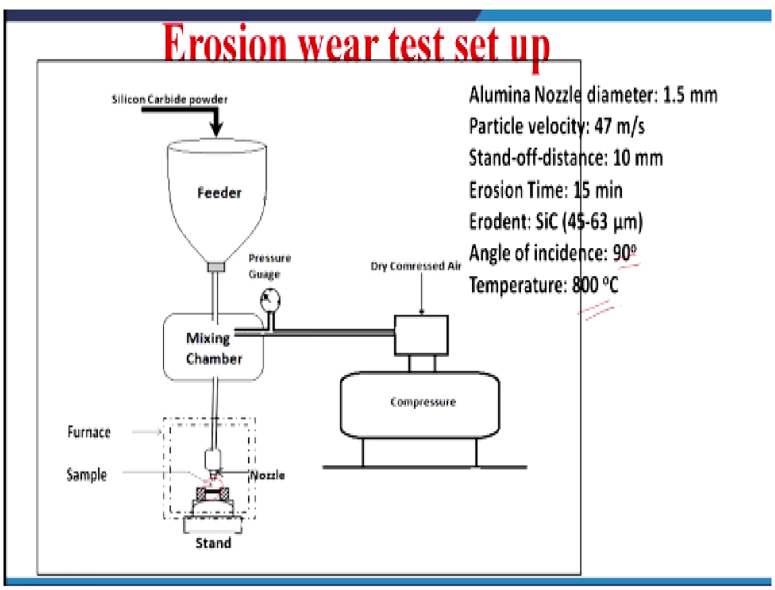

So, we use the erosion wear test set up where the silicon carbide powder used as a erodent which was mixed with the air and then the mix; and the mixture of these air and the particle allowed to erode the sample and the sample can be tilted in such a way that the erodent makes an angle with the surface of the sample so, we studied these investigation at a fixed angle of 90 degree and a fixed temperature of 800 Celsius, right.

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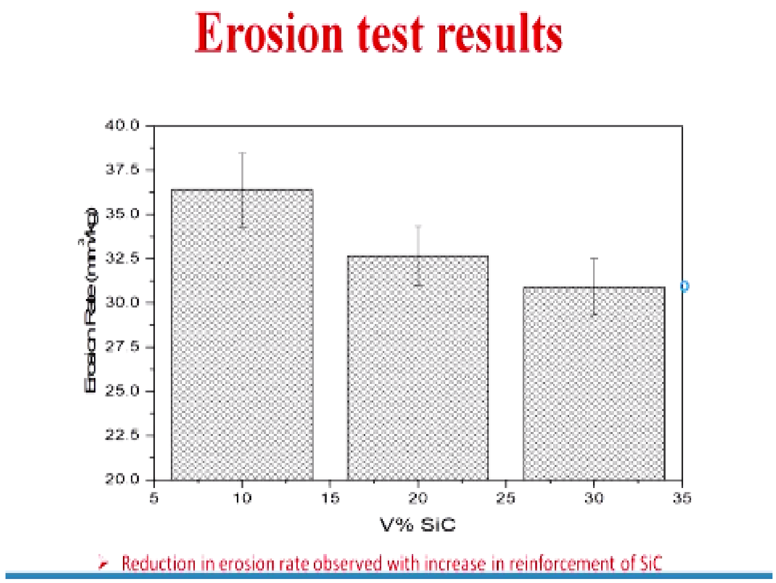

So, erosion test results, (()) (10:41) to (()) (11:47) - NO AUDIO/VIDEO. So erosion rate is the volumetric material removal divided by the amount of erodent used, so we can see there is a reduction in the erosion rate observed with the increase in the silicon carbide content.

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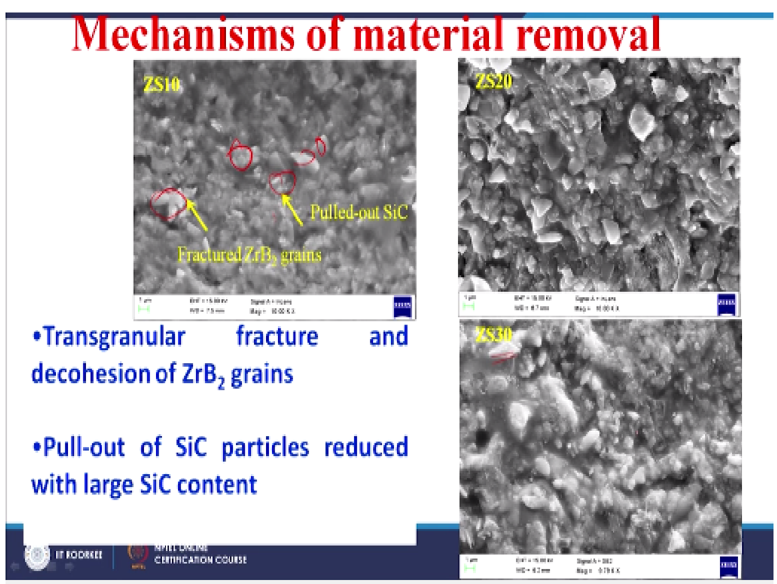

The mechanisms of the material removal can be understood by studying the one surfaces, so all these material removal occurred by these trans granular fracture and de-cohesion of the ZrB2 grains and then the pull out of these silicon carbide particles, you can see there is a grain fracture and then removal, right and then there are small particles which are silicon carbide particles, they are pulled out.

So, the trans granular fracture and de-cohesion of ZrB2 grains are observed and pull out of these silicon carbide particles is reduced with increase in the silicon carbide content that means, the composite having large amount of silicon carbide showed a relatively lesser pull out of the silicon carbide particles.

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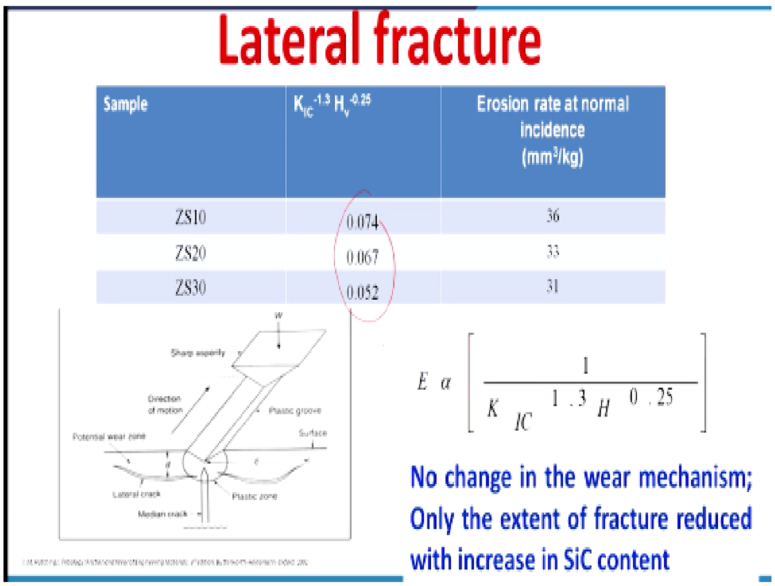

So, lateral fracture model shows that whenever there is a sharp object sliding over on the brittle material, their generate a plastic deformation zone and then upon releasing this load that means upon moving of this particles from this contact to contact, so there generates a lateral crack, so median cracks and lateral cracks are generated because of these impingement and then sliding, so this energy is consumed in making this cracks.

So, the lateral fracture model show that this parameter in terms of the fracture toughness and hardness is inversely proportional to the erosion rate, so we just observed there is a linear relation with the erosion rate at that normal incidence to this erosion parameter, so no change in the wear mechanism can be understood, this is 1.3, this is .25, this is actually -1.3, -.25, so as this parameter is decreased, you see the decrease in the erosion rate, right.

So, this decrease in the erosion rate shows that there is no change in the wear mechanism, it is simply the lateral fracture induced wear, so what is the difference from ZS10 to ZS30, it is only the extent of the fracture nothing else.

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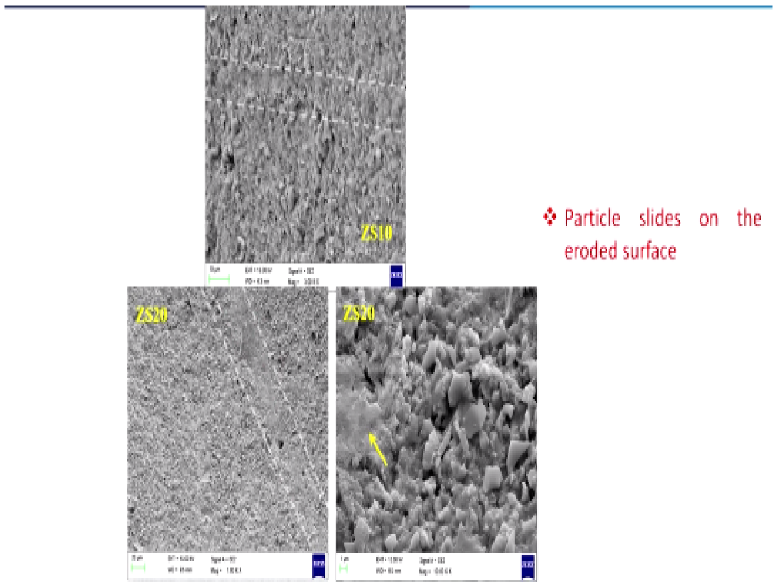

But very interestingly, the conical crater region show also a smoother regions like particles are sliding on the surface, so this is only possible when there is a smoother region on the surface, so like this.

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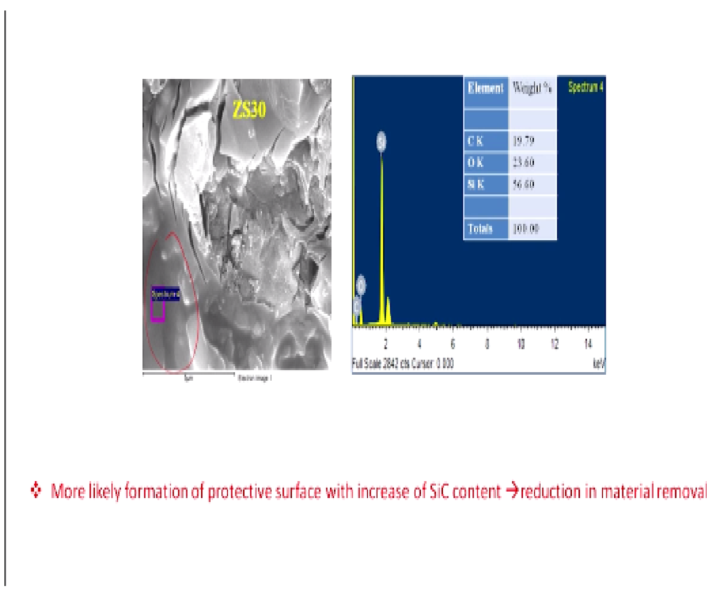

So, in addition to that EDS analysis also show that smoother region is an oxide region, right, so when you have a larger amount of silicon carbide in the composite, there is more likely formation of these smoother region which actually protects the surface from the further material removal, so if you have larger amount of silicon carbide, there is a chance that large amount of such a protective surface layer covering the surface.

So, you can see the fracture of this grain, actually is restricted when there is such a protective surface, the protective surface is rich with their oxides.

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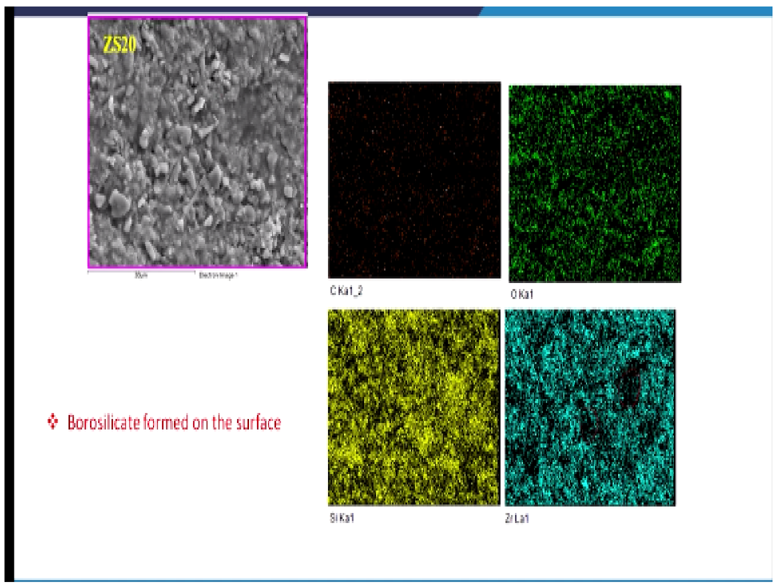

So, the x-ray mapping of these eroded surface also show boron, silicon and oxygen present on the surface, so you can see here this zirconia; zirconium is not present here, right so whereas the silicon and oxygen is present, so it actually indicates as a silicon and oxygen are because of the limitation from the EDS analysis, the boron cannot be analysed thoroughly.

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Erosion on oxidized surface

$$SiC + 1.5\ O_2 = SiO_2 + CO$$
$$ZrB_2 + 2.5\ O_2 = ZrO_2 + B_2O_3(l)$$

Erosion on surface having viscous boroslicate!!

Fahrenholtz J. Am. Ceram. Soc., 90 [1] 143–148 (2007)
Monteverde, F. and Bellosi, A., J. Electrochem. Soc., 2003, 150, B552–B559

So, from the literature, we can also understand the silicon carbide has a nascent oxygen, so it actually has a nascent silicon oxide or in oxidised conditions like that we used here that we used in a high temperature 800 silicon carbide converts to silicon oxide, so in either case there is a silicon oxide availability on the surface and ZrB2 also in high temperature conditions oxidises and then forms a ZrO2 and B2O3.

B2O3 being a low melting compound, it actually is a liquid, so this B2O3, so this boron oxide is also present in the silicon oxide is also present, so these erosion is actually occurring on the surface with the viscous boride or silicate or borosilicate.

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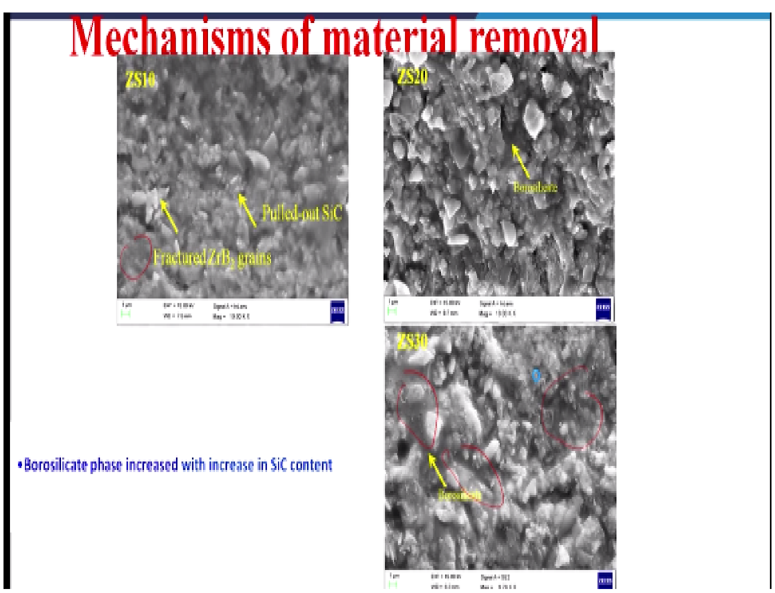

So, again revisiting the eroded surface also show so, show such borosilicate formation is actually increased with the increase in SiC content in the composite, so we can understand that because of the presence of such a viscous borosilicate, the further wear is restricted, so the presence of such a borosilicate formation is more likely when you have a larger amount of silicon carbide in the composite.

So that you will get a larger amount of silicon which reacts with the borate and then forms a borosilicate, so with increase in silicon carbide content in the composite, there is viscous borosilicate formation, so we can see such a viscous phase is more available on the ZS30 than the ZS10, so this is actually stopping further wear that means, when the surface is protected with such a layer, the further wear is restricted.

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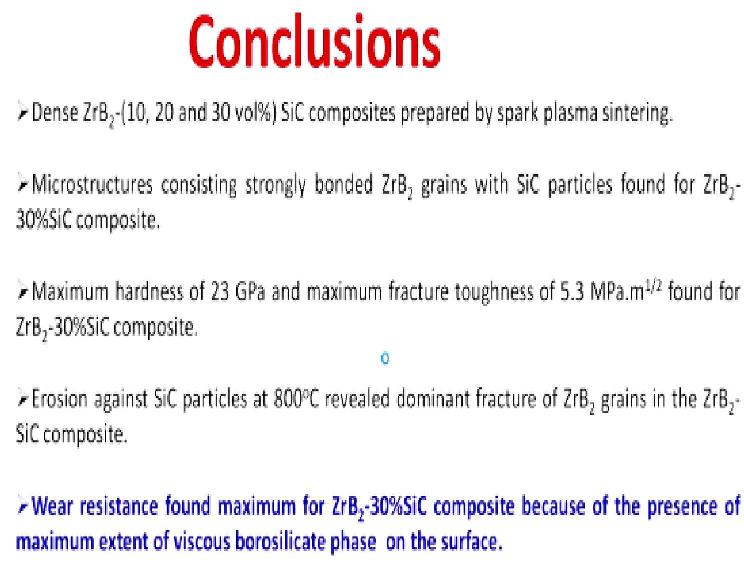

So, the conclusions from the present study are like the dense composites with ZrB2 and 10, 20, 30 volume percent silicon carbide were prepared by spark plasma sintering, the density was more than 98%, the microstructures consisting strongly bonded ZrB2 grains with silicon carbide particles found for that composite with the larger amount of silicon carbide in this present investigation that is ZrB2 with 30% silicon carbide.

Maximum hardness of 23 gigapascal and a maximum fracture toughness of 5.3 mpa root meter is found for that composite again having a large amount of silicon carbide that is in this investigation, ZrB2 with 30% silicon carbide, when they were subjected to erosion, again has to silicon carbide particles at high temperature of 800 Celsius revealed dominant fracture of ZrB2 grains in the ZrB2 SiC composites.

When you have a viscous borosilicate face formed on the surface, the fracture is restricted right, so that is how we saw when this fracture of this ZrB2 grain is actually restricted when there is a such a oxide surface is available, so we can understand the wear resistance is found maximum for the composite having larger amount of silicon carbide in these present investigation the ZrB2 with 30% silicon carbide.

This is because of the presence of maximum extent of viscous borosilicate face on that surface, so this particular study showed at high temperature, these composites with larger amount of silicon carbide can restrict wear, so ZrB2 SiC composites with larger amount of SiC content can be used for such a high temperature erosion wear conditions, thank you.