Surface Engineering for Corrosion and Wear Resistance Application
Prof. Jyotsna Dutta Majumdar
Department of Metallurgical and Materials Engineering
Indian Institute of Technology, Kharagpur

Lecture – 44
Thermal Spray Deposition – IV

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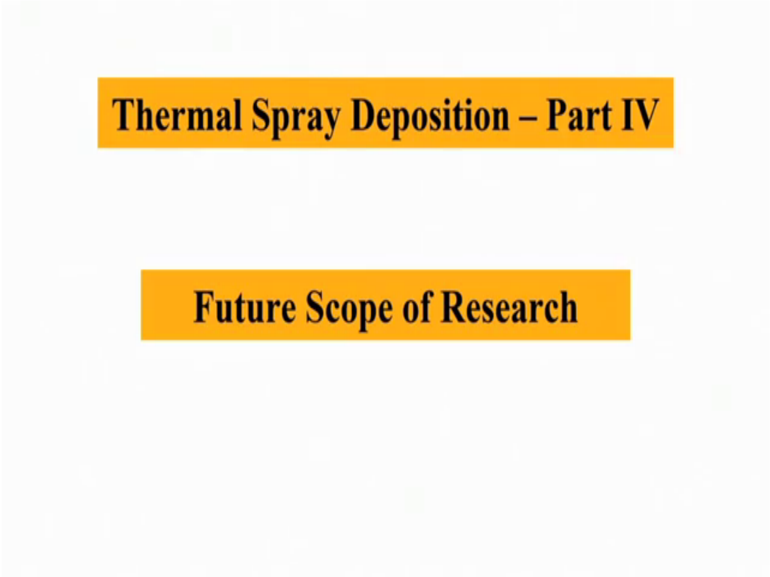

Thermal Spray Deposition – Part IV

Future Scope of Research

Welcome to part IV of Thermal Spray Deposition technique, where we will discuss about the scope of research and also how to plan for the research studies of different materials development by thermal spray deposition route. In this particular talk I will discuss about the research results on development of two different types of coating; one is thermal barrier coating and another one is typical bioactive coating for implant applications.

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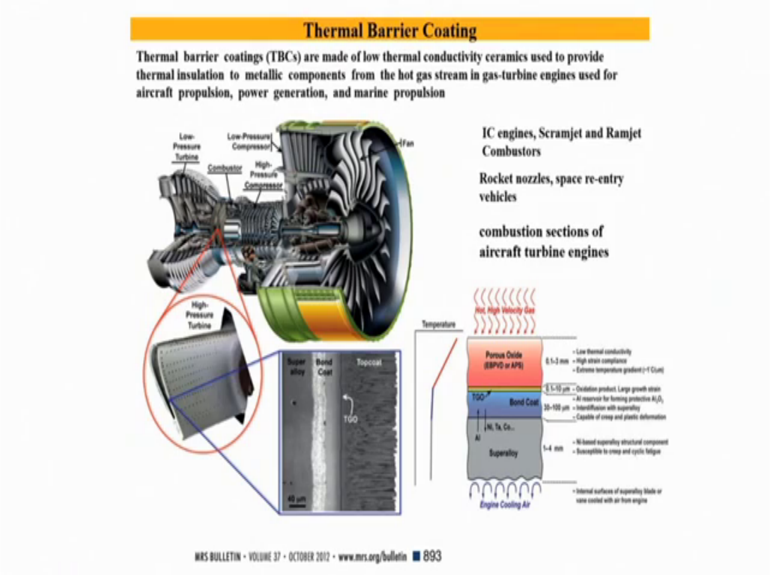

Thermal Barrier Coating

Thermal barrier coatings (TBCs) are made of low thermal conductivity ceramics used to provide thermal insulation to metallic components from the hot gas stream in gas-turbine engines used for aircraft propulsion, power generation, and marine propulsion

IC engines, Scramjet and Ramjet Combustors

Rocket nozzles, space re-entry vehicles

combustion sections of aircraft turbine engines

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So, initially I will discuss about the thermal barrier coating. So, as I mentioned you in the last slide that thermal barrier coating is usually applied on the turbine blades and nozzles where you are looking for very high temperature oxidation resistance property. And there you look for a thick ceramic layer on the surface of the substrate which is nothing but a super alloys, maybe nickel based superalloys or cobalt based superalloys for the applications where for the different applications as you are looking for.

And that coating is developed onto the surface of the superalloy and before that you apply a very thin bond coating made of conicraly which offers the high temperature oxidation resistance property. And that oxide based ceramics offer that thermal barrier property or acts as insulating barrier for reducing the effective operating temperature of the substrate.

So, usually these coating is this is known that this particular top coating is applied by electronic physical vapour deposition technique or by air plasma spraying technique. But each and every technique is having its own advantages and disadvantages. The advantage of air plasma spraying technique, cobalt ebpvd is that, air plasma spraying technique is more flexible technique.

By this particular technique you can have all lateral cracks and these lateral cracks acts as a kind of acts as the centers where, stress can be relaxed very nicely. So, when the component is subjected to like thermal stress that cyclic thermal stress then those stresses can be arrested very nicely. On the typical plasma sprayed defective part lie lateral cracks whatever are present on the surface.

Air plasma spray is quite cheap and easy to operate, you get thicker coating by air plasma spraying than ebpvd and it is tougher than that of electron beam physical vapor deposition technique. So, you can for having the flexible composition on the coated layer for having different types of coating. Usually, people choose the plasma spray deposition technique, prefer to have plasma spray deposition technique to electron beam physical vapor deposition technique.

So, it is known that this technique is applied for a TBC development. On the other hand if you talk about bond coat; bond coat may be developed by plasma spraying process, but when you develop that bond coat by plasma spraying process these chance of lot of porosity porosities which are arrested in the bond coat. So, usually what you do is that you develop the bond coat by typical is your spraying technique.

So, when you develop it by is your spray technique by you get very dense coating and that dense coating is capable of improving the properties of the component to a large extent, because it offers superior corrosion resistance and high temperature oxidation resistance property of the material. So, if you see that temperature because the temperature profile through the coating because of the application of the coating, you will find that and maybe designing of the coating.

You will find that this is superalloy which is having the bond coat of the thickness 30 to 100 micron. Then top coat thickness is 100 to 300 3000 micrometer 100 to 3000 micrometer and then usually the TQO layer is having maximum thickness of 0.1 to 10 micron. This is nothing but oxidation product and the temperature increases that from the surface temperature decreases and then it is minimum at the bond coated superalloy substrate. So, you will find that this is the combinations and this is very quite established that people do use these techniques for this specific purpose.

Now, if you are interested to develop newer kind of materials for these thermal barrier applications or newer varieties of coatings having Taylor properties, then you have to choose off; you have to think of choosing superior materials. So, superior materials in this regard include lanthanum staminized lanthanum, stabilized zirconia or the composites of yttria stabilized zirconia and lanthanum stabilized zirconia and also you can add different rare earth element to a large extent in the bond coat.

And then prepare the bond coat of different completely different composition and then develop it by is your spraying technique. So, those are the areas where lot of researchers are working and then a new under materials are developed for these particular purpose.

So, in these particular research studies we what we I would say briefly explain or say as some of our research experience on the development of thermal barrier coating. So, where our newer approach was to develop the grader coat graded coating instead of the monolithic composite monolithic ceramic coating as the thermal barrier coating to have the higher toughness and also superior properties of the coating.

So, where what we did is that we basically use the coniraly standard powder as the bond coat and for top coat instead of having the yttria-stabilized zirconia. Monolithic coating are used a combination of yttria-stabilized zirconia and the and coniraly in a graded fashion. So, that near to the bond coat the composition was 90 percent bond coat plus 10 percent top coat as you go ahead you will find that the composition of the bond coat percentage of bond coat decreases and at the surface it is 100 percent top coat.

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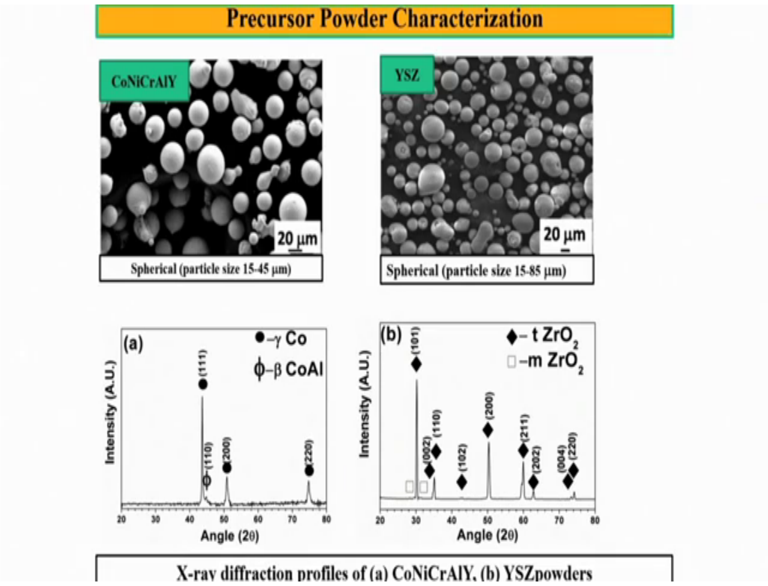
Precursor Powder Characterization

Spherical (particle size 15-45 μm)

Spherical (particle size 15-85 μm)

X-ray diffraction profiles of (a) CoNiCrAlY, (b) YSZpowders

So, like that we design the coating and try to see the effect on try to see its effect on oxidation resistance as well as overall service life of the component. So, as I mentioned you that in this particular say any process of thermal spray deposition, your precursor coating precursor may be in the form of powder or may be in the form of wire or may be in the form of rod. But when you talk about plasma spray deposition process then naturally the precursor coating precursor should always be in the form of powder.

So, particularly in those case for example, where we use that yttria-stabilized zirconia as powder; so, when you develop the; when you started developing the yttria-stabilized zirconia top coat by plasma spray deposition technique. This yttria stabilized zirconia gas atomized powder was used as precursor powder which contains mostly a tetragonal zirconia; if your monoclinic zirconia is also observed and monoclinic zirconia peaks are also observed. On the other hand bond coat was conicraly so, where we get only gamma as well as a few beta peaks were also observed.

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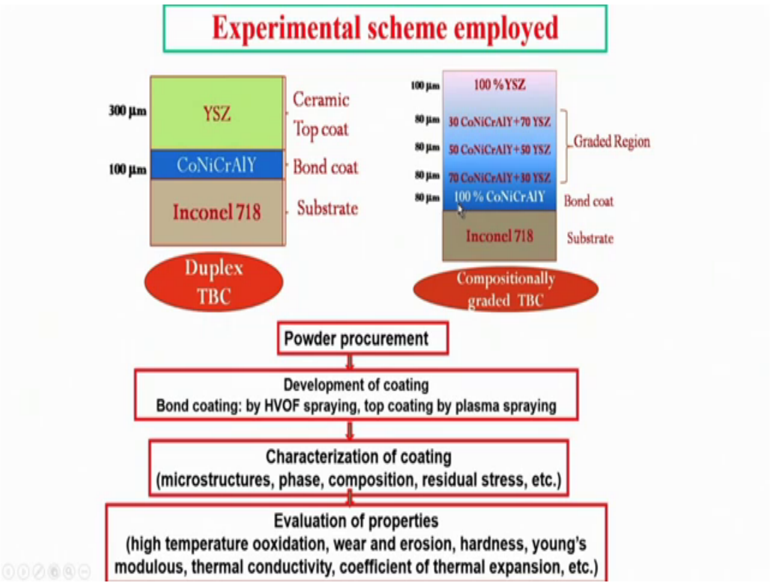

Experimental scheme employed

Powder procurement

Development of coating
Bond coating: by HVOF spraying, top coating by plasma spraying

Characterization of coating
(microstructures, phase, composition, residual stress, etc.)

Evaluation of properties
(high temperature ooxidation, wear and erosion, hardness, young's modulous, thermal conductivity, coefficient of thermal expansion, etc.)

So, these particular coating was developed by plasma spraying, this coating was developed by (Refer Time: 08:26) spraying. So, the coating design was like that. So, this is a newer approach which we followed. Basically, instead of having the monolithic coating we had graded coating so, where 100 percent conicraly, 70 percent conicraly plus 30, 50-50; I mean we developed 4 layers, each layer is having thickness of 80 micron.

So, total and final layer thickness was 100 micron so, bond coat thickness was around 80 micron and total top coat thickness was around 240 4 3 340 micron 340 to 350 micron.

So, and each layer was having the similar thickness; so, what we did is that we just developed both the kind of coating in order to so, the effect of the composition of radiation on the microstructure composition and properties. So, the states which you are followed or which is usually followed for these kind of experiment was that you have to procure powder, then you have to develop the coating.

In order to characterize the coating, then evaluation of properties in terms of high temperature oxidation, wear erosion, hardness, Young's modulus, thermal conductivity, coefficient of thermal expansion these all properties were evaluated and finally, we try to compare the properties of the both coating to large extent.

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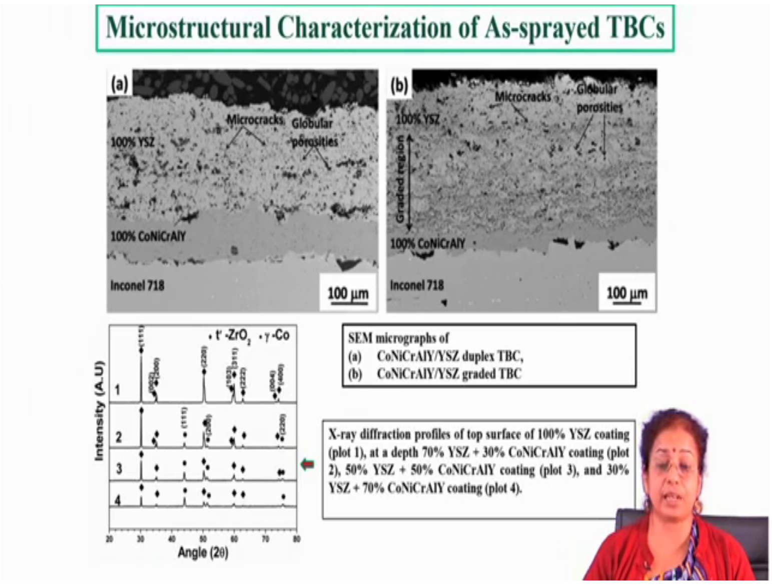

Microstructural Characterization of As-sprayed TBCs

SEM micrographs of
(a) CoNiCrAlY/YSZ duplex TBC,
(b) CoNiCrAlY/YSZ graded TBC

X-ray diffraction profiles of top surface of 100% YSZ coating (plot 1), at a depth 70% YSZ + 30% CoNiCrAlY coating (plot 2), 50% YSZ + 50% CoNiCrAlY coating (plot 3), and 30% YSZ + 70% CoNiCrAlY coating (plot 4).

So, if you see that coating thermal barrier coating microstructure cross section you will find that these particular coating contains lot of porosities as well as the cracks in the lateral dimension. So, those cracks are present because those cracks as I mentioned you they are essential because they basically they acts as a kind of points of stress relaxation.

So, whenever these lateral cracks are present naturally, you will find that whatever thermal stresses are developed, they get relaxed very nicely over the crack points. And, because of the very high large stress actually there is a just change in monoclinic to tetragonal to monoclinic structure and by the structural transformation the crack tip is also toughened. So, during the process itself you will find that yttria-stabilized zirconia gets toughened and it offers the further improvement in the toughness.

So, in the monolithic coating we had this particular yttria-stabilized zirconia layer and conicraly layer you will find there is not much porosities because it has been developed by US spraying route and you get 100 percent days coating. In the case where you use the graded coating, there you find that degree of porosities where little bit lower than that of monolithic coating, and you will find that there are presence of both metallic as well as ceramic component.

And ceramic component content increases as we go on increasing from day towards the surface because of the change in the composition. So, this is also visible in the X-ray diffraction profile.

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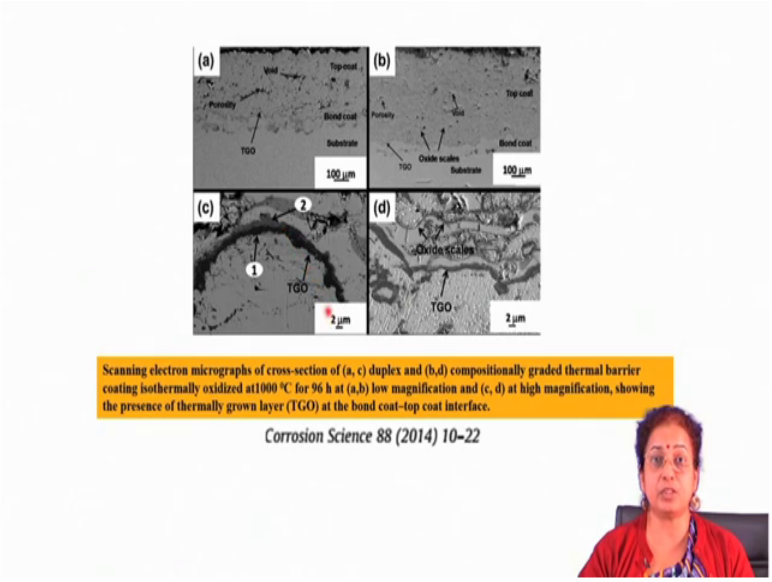

Scanning electron micrographs of cross-section of (a, c) duplex and (b,d) compositionally graded thermal barrier coating isothermally oxidized at1000 °C for 96 h at (a,b) low magnification and (c, d) at high magnification, showing the presence of thermally grown layer (TGO) at the bond coat–top coat interface.

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So, you will find that cross section when the microstructure this kind of coating is subjected to high temperature oxidation, you will find that there is a very thin TGO formation at the interface. And TGO thickness is quite low and that TGO thickness in fact, increases with temperature as well as time of the oxidation.

So, usually you observe the or maybe you see the performance of the coating when you do high temperature oxidation study. And usually performance of the coating in terms of the micro structural change, if you would like to see you will find that from the surface of the coating, you will find no signature of the oxidation because that is already oxide layer.

And also mentioned you that particular ceramic layer or insulating layer or thermal barrier coating actually does not offer the high temperature oxidation resistance property. But high temperature oxidation resistance property is usually offered by the typical bond coat which you are using for the top coat development. Because bond coat offers high temperature oxidation resistance and as a result of which whatever oxide scale forms that forms at the interface between the bond coat and top coat.

So, you must study the interface very meticulously and measure the thickness of the TGO layer as a function of time and temperature to study the oxidation behavior of this kind of coated alloy. It is very much penetrating job because, every time you have to measure the thickness of the oxide layer at the interface not at the surface. So, these interface layer looks like that.

On the other hand if you talk about the radiate coating you find that this TGO layer is not freely forming on a single zone, it is forming all throughout the surfaces wherever it faces the bond coat. So, TGO again is formed inside it is not really continuous layer, it forms at the interface again, it forms at the interface between coating and that of bond coat and that of ceramic layer interface.

So, different layers you will get different TGOs formation. So TGOs, these TGOs actually acts as a kind of a again kind of barrier for the subsequent oxidation in case of graded coating as compared to that of monolithic coating.

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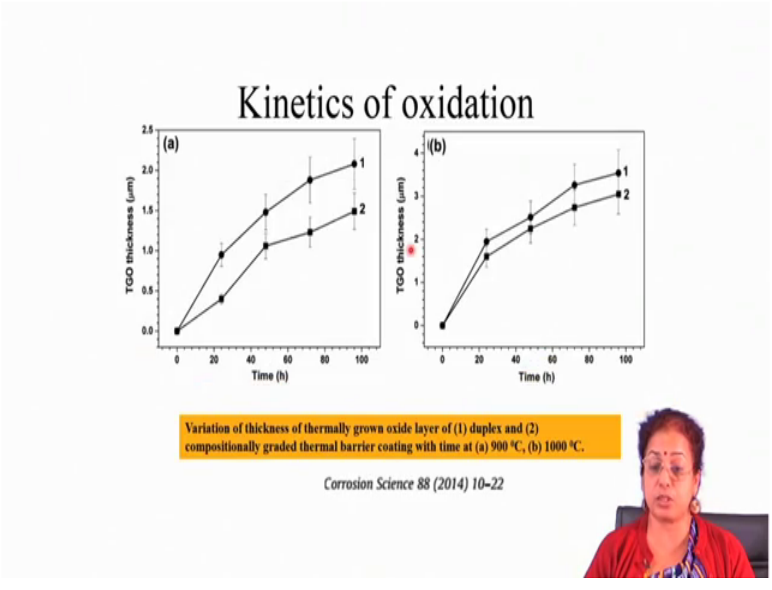

Kinetics of oxidation

Variation of thickness of thermally grown oxide layer of (1) duplex and (2) compositionally graded thermal barrier coating with time at (a) 900 °C, (b) 1000 °C.

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So, if you just measure the kinetics of oxidation for monolithic coating or duplex coating and that of graded coating; you will find that the kinetics of oxidation is much lower in case of graded coating as compared to that of duplex coating, for both the temperatures of oxidation like 900 degree as well as 1000 degree. So, you can understand that by the application of the graded coating, the oxidation resistance property could also be improved which was not earlier known.

Because the main reason behind the improved oxidation resistance property is that there are a lot of interfaces, which are generated because of that interval; because of the inter mixing and spraying of the that ceramic metal mixed layer instead of having only ceramic layer on the top.

So, that interfaces play a very important role because it hinders the transportation of the oxidation or acts as a barrier of oxide barrier for the oxygen transport and as a result of which overall kinetics of oxidation increases when you have the typical graded coating as compared to that of duplex coating. So, now, if you just see the typical activation energy for oxidation in case of duplex coating and graded coating, you will find that it is in fact, much higher than that of duplex coating.

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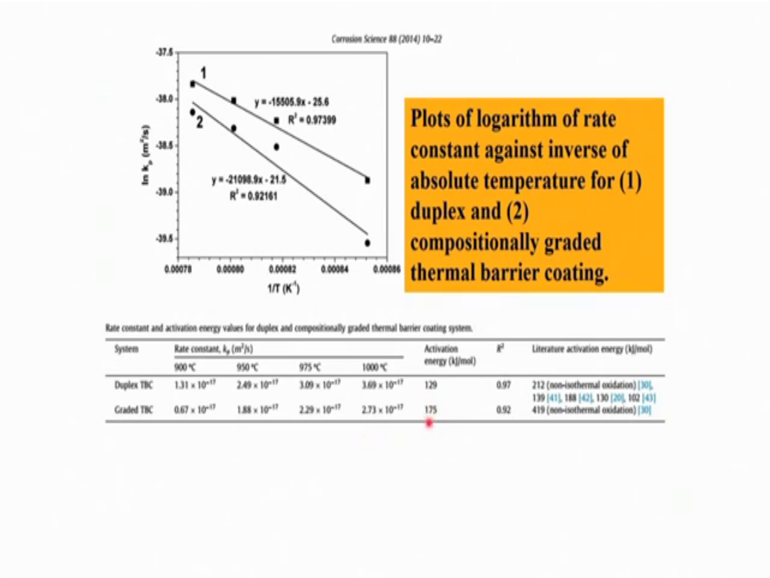

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Plots of logarithm of rate constant against inverse of absolute temperature for (1) duplex and (2) compositionally graded thermal barrier coating.

Rate constant and activation energy values for duplex and compositionally graded thermal barrier coating system.

System	Rate constant, k_p (m^2/s)				Activation energy (kJ/mol)	R^2	Literature activation energy (kJ/mol)
	900 °C	950 °C	975 °C	1000 °C			
Duplex TBC	1.31×10^{-17}	2.49×10^{-17}	3.09×10^{-17}	3.69×10^{-17}	129	0.97	212 (non-isothermal oxidation) [30], 139 [41], 188 [42], 130 [20], 102 [43]
Graded TBC	0.67×10^{-17}	1.88×10^{-17}	2.29×10^{-17}	2.73×10^{-17}	175	0.92	419 (non-isothermal oxidation) [30]

So, duplex coating it was earlier observed that all it was earlier documented that graded coating would be beneficial for improving the toughness of the coating. But, we established that not only toughness, but also high temperature oxidation resistance also increases because of the development of the graded coating in contrast to that of duplex coating.

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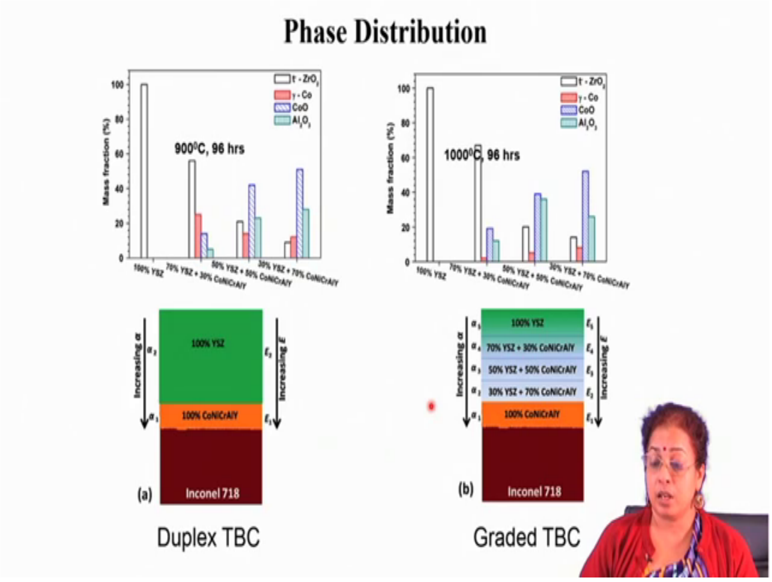

Phase Distribution

Duplex TBC

Graded TBC

Now, when you found their mass distribution; naturally, we find that in case of the duplex coating that typical mass distributions are like only 100 percent duplex coating it is that the tetragonal zirconia. On the other hand in case of after oxidation we get tetragonal zirconia, gamma phase, cobalt oxide, alumina in the oxide scale actually.

And similarly, if you see that in the in case of graded coating again, you will find that in different layer, different phases are forming and this phase distribution is very much dependent on that composition of the each layer. So, but you will find that alumina is forming to a large extent in different layers which basically acts as a barrier to the high temperature oxidation property.

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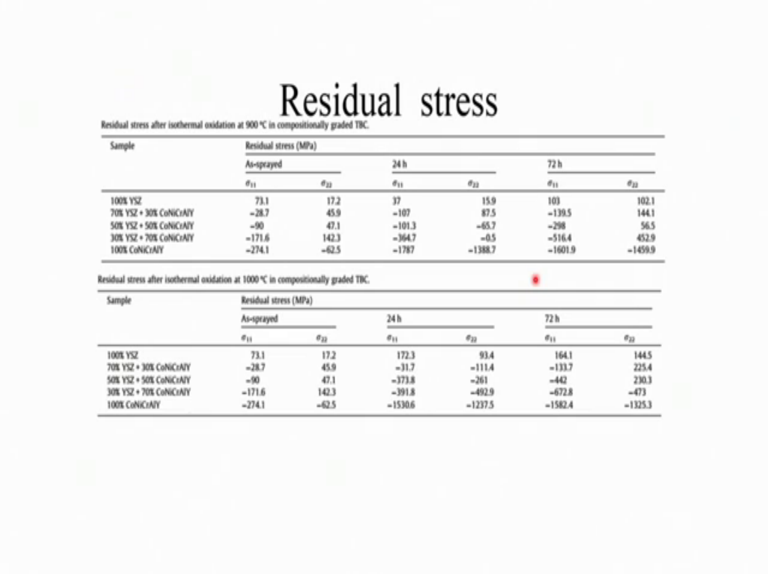

Residual stress

Residual stress after isothermal oxidation at 900 °C in compositionally graded TBC.

Sample	Residual stress (MPa)					
	As-sprayed		24 h		72 h	
	σ_{11}	σ_{22}	σ_{11}	σ_{22}	σ_{11}	σ_{22}
100% YSZ	73.1	17.2	37	15.9	103	102.1
70% YSZ + 30% CoNiCrAlY	−28.7	45.9	−107	87.5	−139.5	144.1
50% YSZ + 50% CoNiCrAlY	−90	47.1	−101.3	−65.7	−298	56.5
30% YSZ + 70% CoNiCrAlY	−171.6	142.3	−364.7	−0.5	−516.4	452.9
100% CoNiCrAlY	−274.1	−62.5	−1787	−1388.7	−1601.9	−1459.9

Residual stress after isothermal oxidation at 1000 °C in compositionally graded TBC.

Sample	Residual stress (MPa)					
	As-sprayed		24 h		72 h	
	σ_{11}	σ_{22}	σ_{11}	σ_{22}	σ_{11}	σ_{22}
100% YSZ	73.1	17.2	172.3	93.4	164.1	144.5
70% YSZ + 30% CoNiCrAlY	−28.7	45.9	−31.7	−111.4	−133.7	225.4
50% YSZ + 50% CoNiCrAlY	−90	47.1	−373.8	−261	−442	230.3
30% YSZ + 70% CoNiCrAlY	−171.6	142.3	−391.8	−492.9	−672.8	−473
100% CoNiCrAlY	−274.1	−62.5	−1530.6	−1237.5	−1582.4	−1325.3

Now, if when we just measure the residual stress distribution in the different layer, we found that residual stress also changes to a large extent in case of duplex as well as graded coating. So, you will find that in compositional graded coating, you will find that 100 percent YSZ residual stress is mostly positive. On the other hand, as we go on increasing the metallic content of the coating, residual stress content, residual stress value just changes from tensile to compressive.

So, metallic incorporation actually also helps in reducing the residual stress level not only reducing the stress level, but also changing the stress value from the tensile to compressive. So, this is very much important because residual stress when is compressive naturally it helps in and improving the resistance to thermal fatigue thermal stock resistance.

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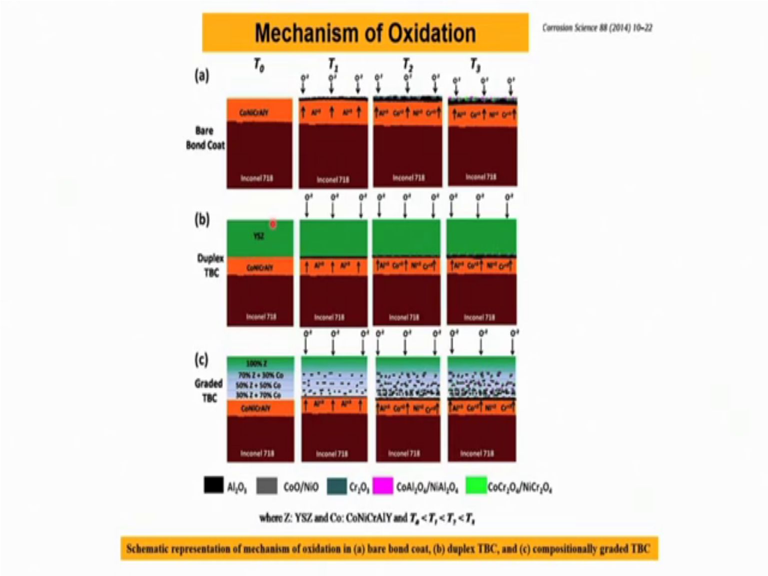

Mechanism of Oxidation

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■ Al_2O_3 ■ CoO/NiO ■ Cr_2O_3 ■ $CoAl_2O_4/NiAl_2O_4$ 🟩 $CoCr_2O_4/NiCr_2O_4$

where Z: YSZ and Co: CoNiCrAlY and $T_0 < T_1 < T_2 < T_3$

Schematic representation of mechanism of oxidation in (a) bare bond coat, (b) duplex TBC, and (c) compositionally graded TBC

So, now we propose the mechanism of oxidation where we propose that the presence of metal oxide at the metal ceramic interface acts as a barrier for counter ionic transportation and by that process it basically there are also a lot of spinel formation. So, these particular spinel and different oxides help in increasing the kinetic energy of the oxidation and hence the rate of oxidation decreases to a large extent.

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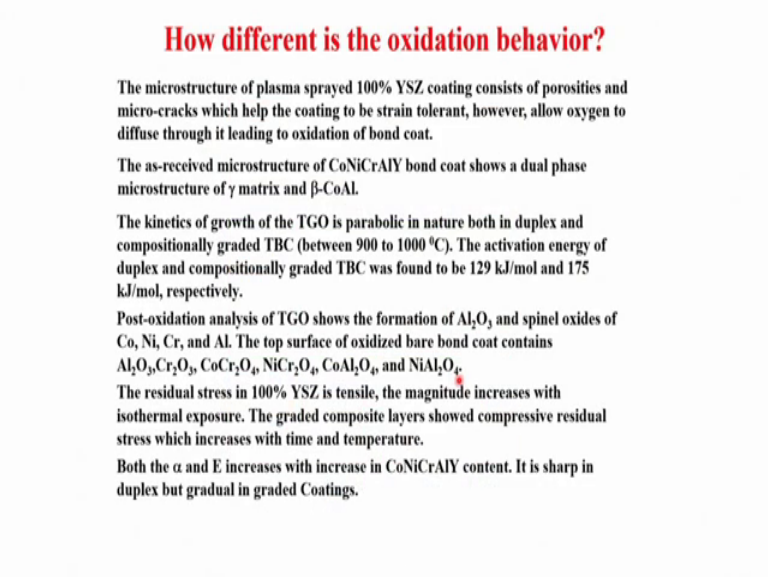

How different is the oxidation behavior?

The microstructure of plasma sprayed 100% YSZ coating consists of porosities and micro-cracks which help the coating to be strain tolerant, however, allow oxygen to diffuse through it leading to oxidation of bond coat.

The as-received microstructure of CoNiCrAlY bond coat shows a dual phase microstructure of γ matrix and β-CoAl.

The kinetics of growth of the TGO is parabolic in nature both in duplex and compositionally graded TBC (between 900 to 1000 ^{0}C). The activation energy of duplex and compositionally graded TBC was found to be 129 kJ/mol and 175 kJ/mol, respectively.

Post-oxidation analysis of TGO shows the formation of Al_2O_3 and spinel oxides of Co, Ni, Cr, and Al. The top surface of oxidized bare bond coat contains Al_2O_3,Cr_2O_3, $CoCr_2O_4$, $NiCr_2O_4$, $CoAl_2O_4$, and $NiAl_2O_4$.

The residual stress in 100% YSZ is tensile, the magnitude increases with isothermal exposure. The graded composite layers showed compressive residual stress which increases with time and temperature.

Both the α and E increases with increase in CoNiCrAlY content. It is sharp in duplex but gradual in graded Coatings.

So, now we can does notable conclusions of that work was that the microstructure of the 100 present YSZ coating consist of porosities and micro cracks which help in coating to be strain tolerant; however, the oxygen ingress is there which leads to oxidation of the bond coat. On the other hand when we have the combination of CoNiCrAlY and YSZ it reduces the quantity of oxygen transported towards the bond coat.

Kinetics of growth of TGO is parabolic in nature and activation energy of duplex and naturally because of the adhesion we could have the higher kinetic energy of the oxidation. And post oxidation analysis, so lot of spinel which actually help in reducing the kinetic; reducing the kinetics of oxidation further or increases the activation energy of the oxidation. And residual stress also is reduced to a large extent and changes from tensile to compressive because of the adhesion graded layer formation.

And we also found that the coefficient of thermal expansion and E value increases with increase in the CoNiCrAlY content and naturally it helps in reducing the stress level. So, like that we also try to develop the yttria stabilized zirconia and yttria-stabilized zirconia and lanthanum mixture. And observe that these composite coating offer superior oxidation resistance property than that of the typical duplex coating.

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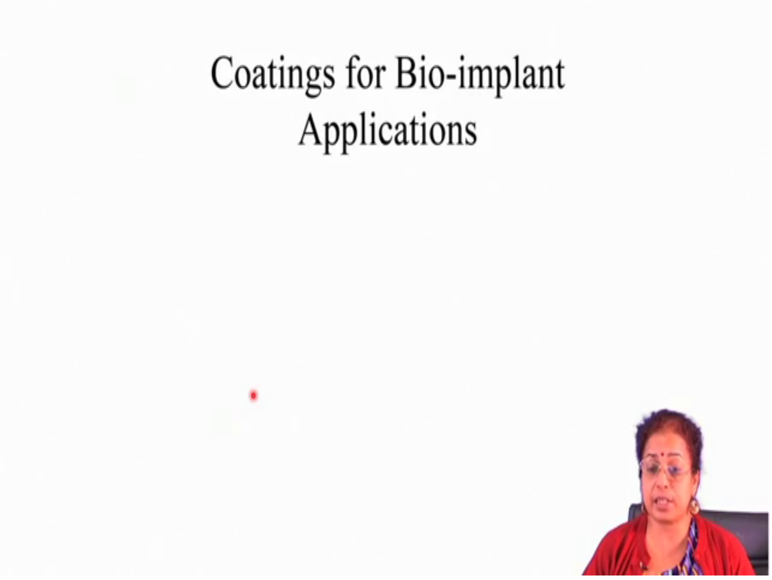

Coatings for Bio-implant Applications

In another example, I will show you that is coatings for bio implant application.

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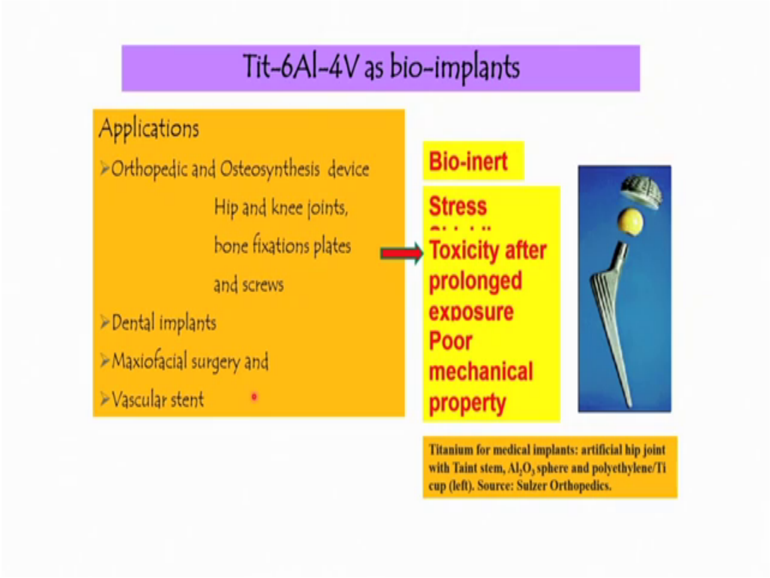

Tit-6Al-4V as bio-implants

Applications

- Orthopedic and Osteosynthesis device
  - Hip and knee joints,
  - bone fixations plates
  - and screws
- Dental implants
- Maxiofacial surgery and
- Vascular stent

Bio-inert

Stress

Toxicity after prolonged exposure

Poor mechanical property

Titanium for medical implants: artificial hip joint with Taint stem, Al_2O_3 sphere and polyethylene/Ti cup (left). Source: Sulzer Orthopedics.

So, this is a kind of bioactive coating, this was applied on Ti 6-4 substrate. So, Ti 6-4 is a very interesting material for bio-implant application, but problem with that Ti 6-4 is that it is bio-inert in nature, as a result of which there is no spontaneous or c integration on the surface of Ti 6 4 and though it is having lot of applications in different implants. For example, hip and knee joints bone fixation plates, screws dental implants, but because of its 4 bio-osseo that osseo integration property; usually, prior to that Ti 6-4 applying as implant inside the human body people go for a typical hydroxyl apatite hydroxyl apatite coating on the surface, but deep coating technique.

But problem of the hydroxyl apatite coating by dip coating technique is that this particular coating is very much fragile in nature. So, its durability decreases to a large extent and hydroxyl apatite gets dissolved gradually and naturally it reduces the lifetime of the component particularly whenever it is a kind of fixed in plan.

So, if we develop the coating by a plasma spray deposition technique naturally, the coating will be stronger because it is having it is really adhering to the surface of the substrate. And not only that because the presence of lot of porosities on the surface, you find that the there is a mussel adhesion on the surface because of the presence of rough surface. So, it has this possibilities of applications in hip and femoral surface or knee joint surface to a large extent.

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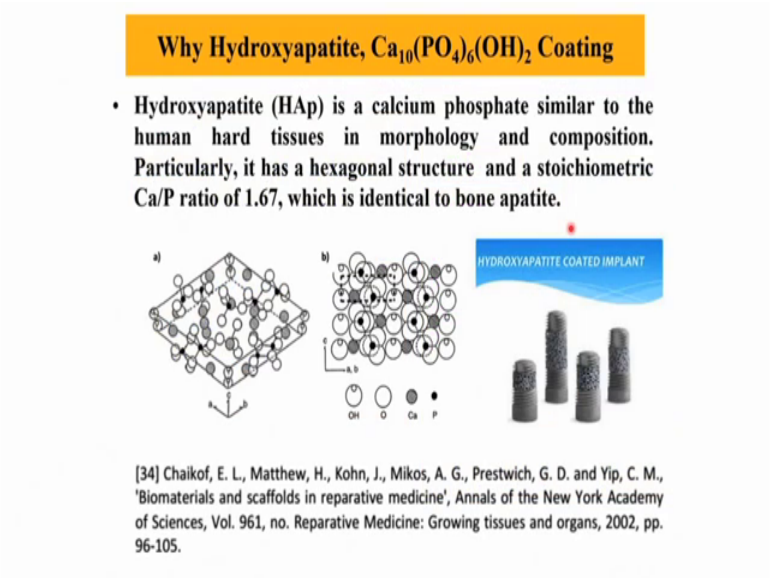

Why Hydroxyapatite, $Ca_{10}(PO_4)_6(OH)_2$ Coating

- Hydroxyapatite (HAp) is a calcium phosphate similar to the human hard tissues in morphology and composition. Particularly, it has a hexagonal structure and a stoichiometric Ca/P ratio of 1.67, which is identical to bone apatite.

[34] Chaikof, E. L., Matthew, H., Kohn, J., Mikos, A. G., Prestwich, G. D. and Yip, C. M., 'Biomaterials and scaffolds in reparative medicine', Annals of the New York Academy of Sciences, Vol. 961, no. Reparative Medicine: Growing tissues and organs, 2002, pp. 96-105.

So, this is typical hydroxyl apatite coating which is very much a bioactive in nature. So, usually it is applied on the implant by dipping technique as I mentioned you. So, that hydroxyl apatite is having that calcium to phosphorus ratio 1.63 67 which is the indication that hydroxyl apatite layer has formed.

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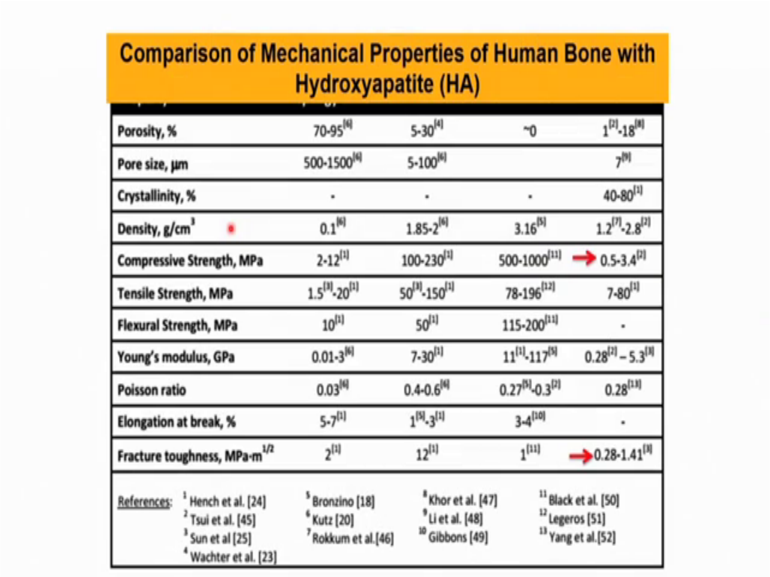

Comparison of Mechanical Properties of Human Bone with Hydroxyapatite (HA)

Porosity, %	70-95[6]	5-30[4]	~0	1[2]-18[8]
Pore size, µm	500-1500[6]	5-100[6]		7[9]
Crystallinity, %	-	-	-	40-80[1]
Density, g/cm^3	0.1[6]	1.85-2[6]	3.16[5]	1.2[7]-2.8[2]
Compressive Strength, MPa	2-12[1]	100-230[1]	500-1000[11]	→ 0.5-3.4[2]
Tensile Strength, MPa	1.5[3]-20[1]	50[3]-150[1]	78-196[12]	7-80[1]
Flexural Strength, MPa	10[1]	50[1]	115-200[11]	-
Young's modulus, GPa	0.01-3[6]	7-30[1]	11[1]-117[5]	0.28[2] – 5.3[3]
Poisson ratio	0.03[6]	0.4-0.6[6]	0.27[5]-0.3[2]	0.28[13]
Elongation at break, %	5-7[1]	1[5]-3[1]	3-4[10]	-
Fracture toughness, MPa-m$^{1/2}$	2[1]	12[1]	1[11]	→ 0.28-1.41[3]

References: [1] Hench et al. [24] [2] Tsui et al. [45] [3] Sun et al [25] [4] Wachter et al. [23] [5] Bronzino [18] [6] Kutz [20] [7] Rokkum et al.[46] [8] Khor et al. [47] [9] Li et al. [48] [10] Gibbons [49] [11] Black et al. [50] [12] Legeros [51] [13] Yang et al.[52]

It is having very good corrosion resistance, it is having very good fracture toughness, porosities are also present which helps in cell adherence and moreover this is bio active in nature.

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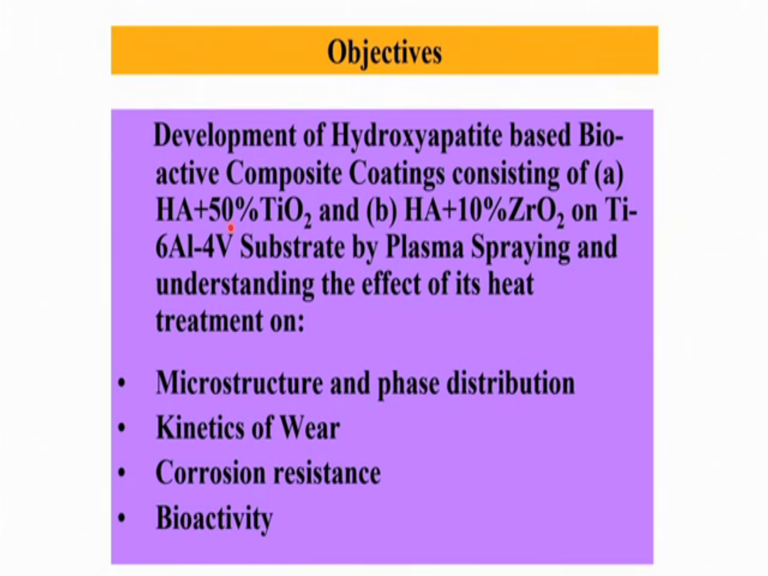

Objectives

Development of Hydroxyapatite based Bio-active Composite Coatings consisting of (a) HA+50%TiO_2 and (b) HA+10%ZrO_2 on Ti-6Al-4V Substrate by Plasma Spraying and understanding the effect of its heat treatment on:

- Microstructure and phase distribution
- Kinetics of Wear
- Corrosion resistance
- Bioactivity

So, in this work we tried to have the; but, one of the biggest problem of hydroxyl apatite is that though it is having good fracture toughness, but not adequate actually. So, it is quite no as compared to that of human bone, particularly when you use it for that those purpose dynamic implant applications, you should have good fracture toughness. So, there the hydroxyl apatite fails.

So, we try to have the increased toughness of the hydroxyapatite and also increase hardness of the hydroxyapatite by adding titanium dioxide as well as zirconia with hydroxyapatite and subsequently developed the coating by plasma spray deposition. So, two different types of coatings were applied again, the composition was earlier attempted, but they did not mention the properties of the coating clearly.

So, in one kind of coating we use hydroxyapatite plus 50 percent titanium, another kind of coating we used hydroxyapatite plus 10 percent zirconia as a coating precursor. And after this is applied after application of the coating in the plasma spray deposition technique we tried to see the microstructure phase, where corrosion resistance as well as bio activity.

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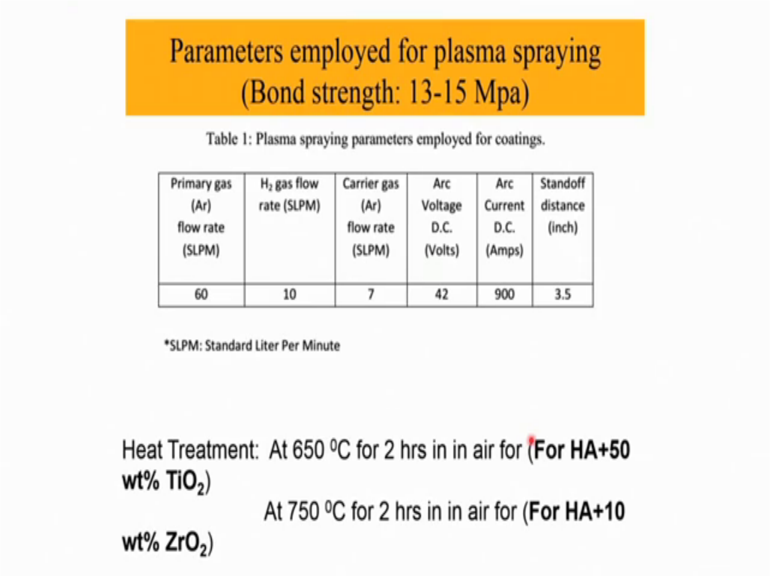

Parameters employed for plasma spraying (Bond strength: 13-15 Mpa)

Table 1: Plasma spraying parameters employed for coatings.

Primary gas (Ar) flow rate (SLPM)	H_2 gas flow rate (SLPM)	Carrier gas (Ar) flow rate (SLPM)	Arc Voltage D.C. (Volts)	Arc Current D.C. (Amps)	Standoff distance (inch)
60	10	7	42	900	3.5

*SLPM: Standard Liter Per Minute

Heat Treatment: At 650 ^{0}C for 2 hrs in in air for (**For HA+50 wt% TiO_2**)

At 750 ^{0}C for 2 hrs in in air for (**For HA+10 wt% ZrO_2**)

So, this is typical the parameters employed for the coating. So, this parameter was the kind of optimal parameter. As I mentioned you whenever you talk about the any deposition technique it is very important that you say the or optimize the parameters properly.

So, parameters which play role in plasma spray deposition there the primary gas flow rate, then hydrogen gas flow rate, then carrier gas flow rate voltage current, standoff distance and the velocity of strain. So, these are the different parameters which play role in determining the quality of the coating. So, we also did another treatment that is heat treatment after the coating.

So, after the spraying we add the different heat treatment that heat treatment was aimed at a retention of the structure of the hydroxyapatite, which after spraying it turns into amorphous. But when we do heat treatment, it converts from amorphous to crystalline and also another reason for heat treatment was to release a stress associated with the coating.

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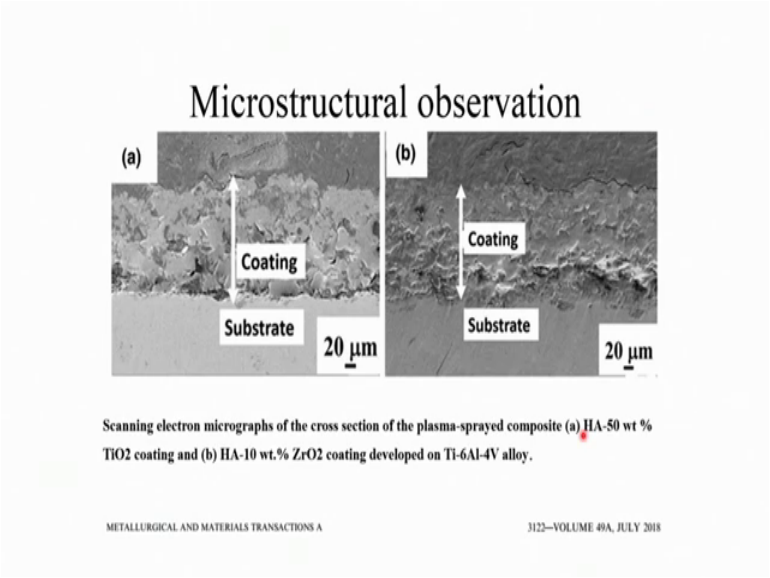

Microstructural observation

Scanning electron micrographs of the cross section of the plasma-sprayed composite (a) HA-50 wt % TiO2 coating and (b) HA-10 wt.% ZrO2 coating developed on Ti-6Al-4V alloy.

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So, if you see the coating carefully you will find that the interface is very strong, you will find there is no porosities or no defects at the interface. Coating thickness varied from 200 micron to 250 micron and in both the cases even though you are using hydroxyapatite plus titania or hydroxyapatite plus zirconia you will not really find those features of the titania or zirconia in a separate way.

So, they mixed properly and got melted and subsequently spread over the surface of the substrate. You can say that there is not much many interfaces present between this coating as well as the hydroxyapatite and zirconia tatana titania.

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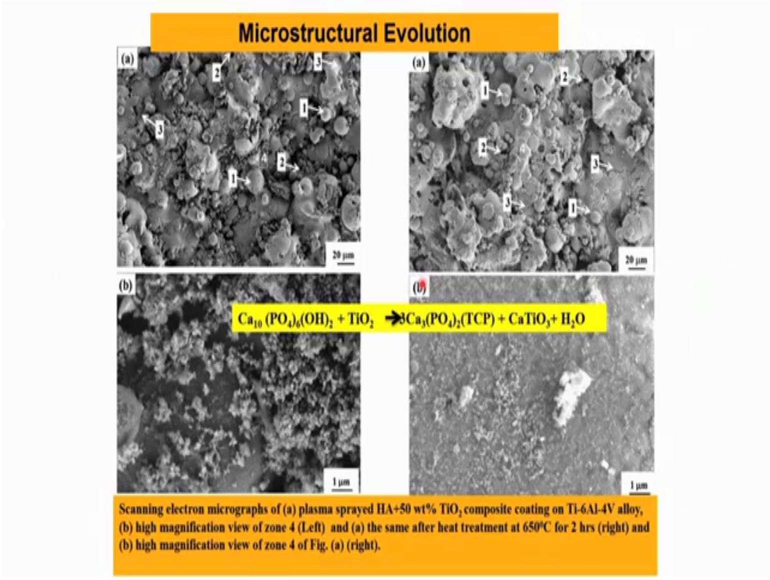

Microstructural Evolution

$Ca_{10}(PO_4)_6(OH)_2 + TiO_2 \rightarrow 3Ca_3(PO_4)_2(TCP) + CaTiO_3 + H_2O$

Scanning electron micrographs of (a) plasma sprayed HA+50 wt% TiO_2 composite coating on Ti-6Al-4V alloy, (b) high magnification view of zone 4 (Left) and (a) the same after heat treatment at 650°C for 2 hrs (right) and (b) high magnification view of zone 4 of Fig. (a) (right).

So, if you see the structure of the surface you will find that here there is a tricalcium phosphate formation, because of the composition of hydroxyapatite and calcium titania deposition in case of hydroxyapatite plus titania coating. On the other hand in hydroxyapatite plus zerconia coating, you will find that there is formation of very fine nano calcium tri calcium zirconate phase formation.

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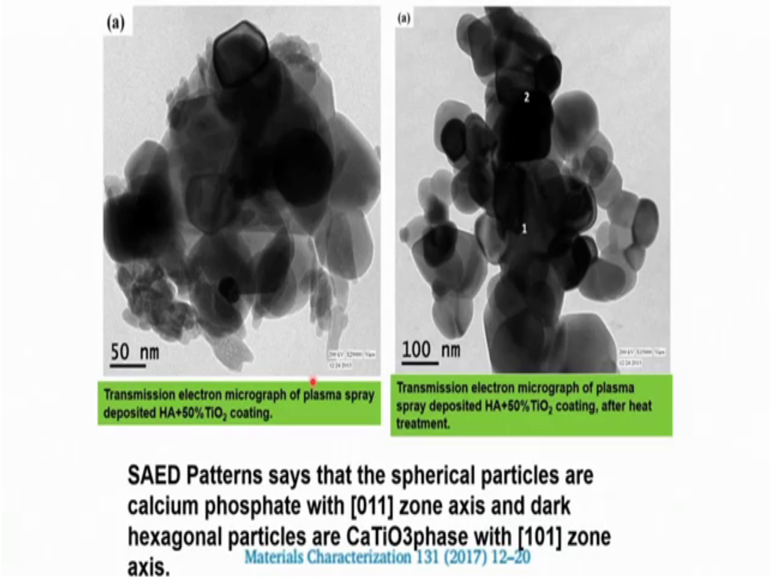

Transmission electron micrograph of plasma spray deposited HA+50%TiO_2 coating.

Transmission electron micrograph of plasma spray deposited HA+50%TiO_2 coating, after heat treatment.

SAED Patterns says that the spherical particles are calcium phosphate with [011] zone axis and dark hexagonal particles are CaTiO3phase with [101] zone axis.

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So, these were actually; these were actually evidence where the transmission electron microscopic analysis. So, whenever you talk about coating you will see the cross section properly. So, that you can make sure that coating is adherent to the surface you can see the microstructure of the cross section as well as microstructure of the top surface properly. So, that you make sure what are the phases present how the microstructure is, because micro structure composition play very important role in determining the bio-activity as well as the corrosion behavior of the material.

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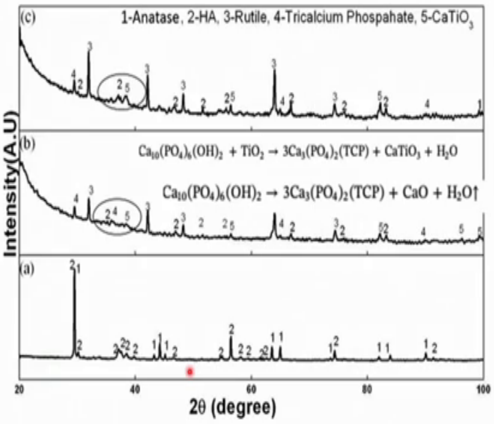

X-ray diffraction profiles of (a) precursor HA + 50 wt% TiO2 powder, the same in (b) as-sprayed state and (c) plasma sprayed followed by heat treatment

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So, that the hydroxyapatite plus titania coating you will find that tri-calcium that in the hydroxyapatite plus zirconia coating you will find that there is formation of calcium zirconate phase and in addition to that tri-calcium phosphate phase.

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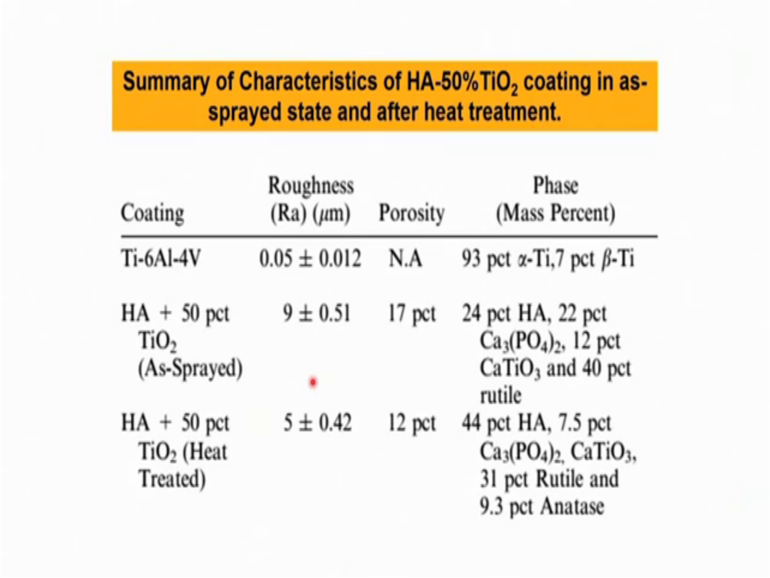

Summary of Characteristics of HA-50%TiO_2 coating in as-sprayed state and after heat treatment.

Coating	Roughness (Ra) (μm)	Porosity	Phase (Mass Percent)
Ti-6Al-4V	0.05 ± 0.012	N.A	93 pct α-Ti,7 pct β-Ti
HA + 50 pct TiO_2 (As-Sprayed)	9 ± 0.51	17 pct	24 pct HA, 22 pct $Ca_3(PO_4)_2$, 12 pct $CaTiO_3$ and 40 pct rutile
HA + 50 pct TiO_2 (Heat Treated)	5 ± 0.42	12 pct	44 pct HA, 7.5 pct $Ca_3(PO_4)_2$, $CaTiO_3$, 31 pct Rutile and 9.3 pct Anatase

So, if you see that microstructure different characteristics of the coating you will find that in 50 percent zirconia aspect condition there is formation of the rough surface, roughness increases about when we did heat treatment of the coating roughness decreases to a large extent. Heat treatment also helps in improving the reducing their porosity percentage and also phase composition was also changed because of the heat treatment.

As I mentioned you that hydroxyapatite when you do spraying it is mostly in amorphous phase, but when you do heat treatment then naturally the crystallinity increases. So, you get more percentage of hydroxyapatite in the coating. So, these roughness is very important in increasing the cell adherence property and porosity is also equally important. But porosity content should not be too high because if it is too high it reduces the toughness to a large extent.

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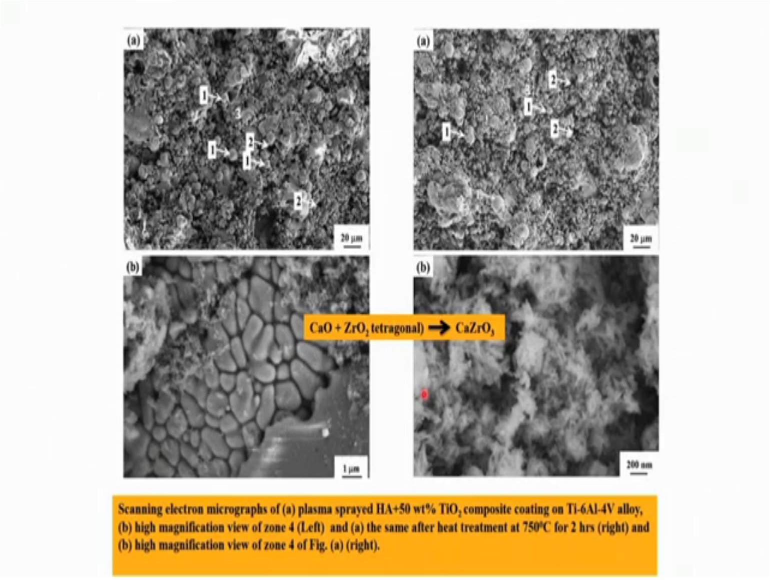

$CaO + ZrO_2$ (tetragonal) → $CaZrO_3$

Scanning electron micrographs of (a) plasma sprayed HA+50 wt% TiO_2 composite coating on Ti-6Al-4V alloy, (b) high magnification view of zone 4 (Left) and (a) the same after heat treatment at 750°C for 2 hrs (right) and (b) high magnification view of zone 4 of Fig. (a) (right).

So, you will find that after heat treatment the how the properties changes actually; so, this is very important because if you just go on doing. This is the case where titanium plus hidroxiappitite plus zirconia coating where you observe that in the coating there are a lot of porosities. And there is also calcium of zirconic phase formation which is nano is in nature because these phases is the in situ formed product. So, because of its in situ formation there are a lot of very much nano structured material on the surface which was again confirmed by transmission electron microscopic analysis.

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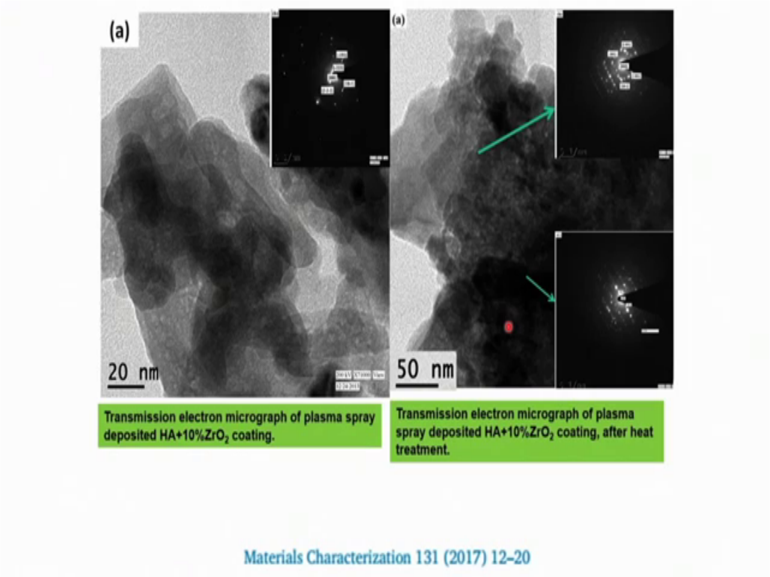

Transmission electron micrograph of plasma spray deposited HA+10%ZrO_2 coating.

Transmission electron micrograph of plasma spray deposited HA+10%ZrO_2 coating, after heat treatment.

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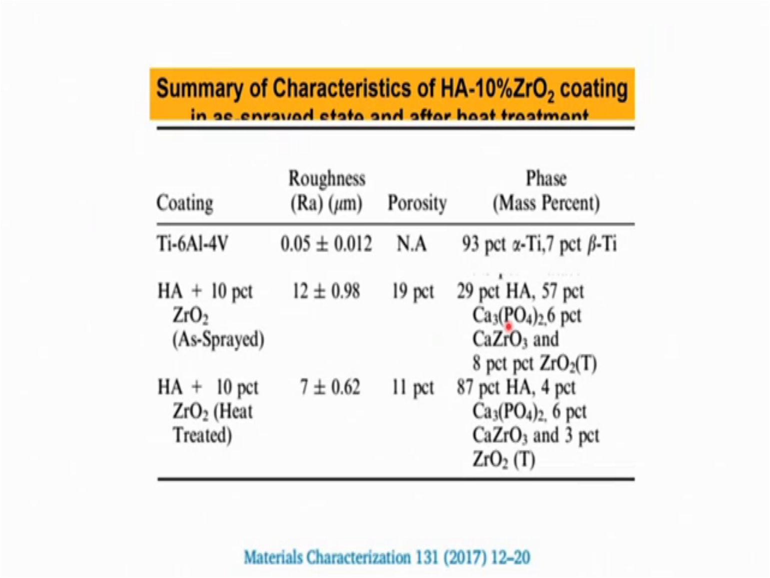

Summary of Characteristics of HA-10%ZrO_2 coating in as-sprayed state and after heat treatment

Coating	Roughness (Ra) (μm)	Porosity	Phase (Mass Percent)
Ti-6Al-4V	0.05 ± 0.012	N.A	93 pct α-Ti,7 pct β-Ti
HA + 10 pct ZrO_2 (As-Sprayed)	12 ± 0.98	19 pct	29 pct HA, 57 pct $Ca_3(PO_4)_2$,6 pct $CaZrO_3$ and 8 pct pct ZrO_2(T)
HA + 10 pct ZrO_2 (Heat Treated)	7 ± 0.62	11 pct	87 pct HA, 4 pct $Ca_3(PO_4)_2$, 6 pct $CaZrO_3$ and 3 pct ZrO_2 (T)

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If you see the characteristics of the zirconia coating, you will find that again porosity and that roughness again changes because of heat treatment. And hence, calcium carbonate hydroxyapatite plus zirconia coating, you find that the degree of amorphousness actually decreases to large extent by heat treatment process.

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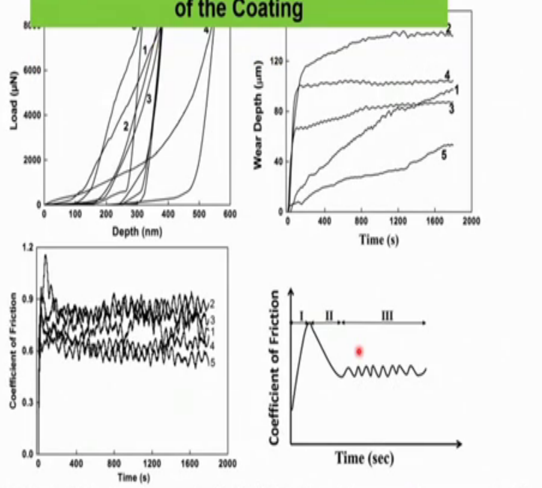
Mechanical and Electrochemical Properties of the Coating



Mechanical behavior of as-received Ti6Al4V (plot 1) and the same plasma sprayed with HA+50%TiO2 (2&3) and HA+10%ZrO2 (4&5) with (3&5) and without (2&4) heat treatment.

So, this is very important because it is having the final effect on the corrosion resistance property. So, when we measured the wear resistance we found that because of that typical hydroxyapatite plus zirconia deposition. We will get significant enhancement in the corrosion wear resistance property; so, because of the hardness achieved in the coated layer.

So, you will find that when we did only hydroxyapatite coating, there we found that hydroxyapatite plus titania coating here, there we found that not much enhancement in the wear resistance was there. But, when you did hydroxyapatite plus zirconia coating after heat treatment we found that I that wear resistors increases.

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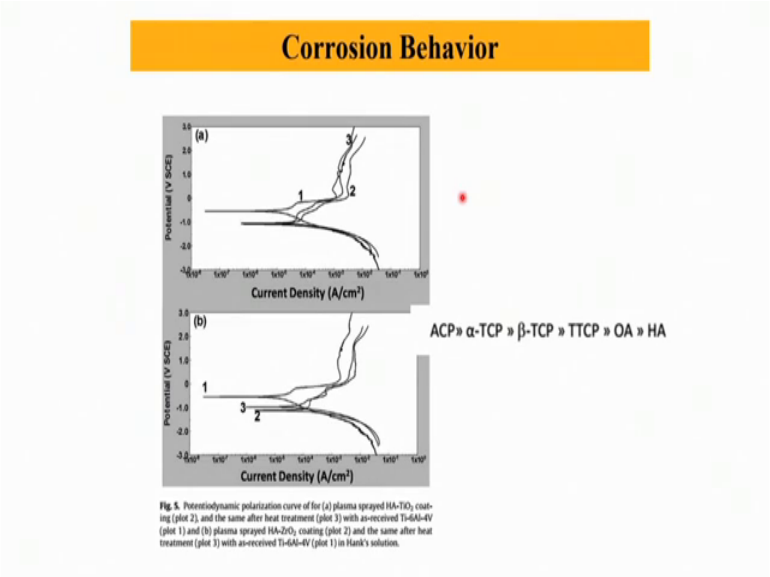

Corrosion Behavior

ACP» α-TCP » β-TCP » TTCP » OA » HA

Fig. 5. Potentiodynamic polarization curve of for (a) plasma sprayed HA-TiO_2 coating (plot 2), and the same after heat treatment (plot 3) with as-received Ti-6Al-4V (plot 1) and (b) plasma sprayed HA-ZrO_2 coating (plot 2) and the same after heat treatment (plot 3) with as-received Ti-6Al-4V (plot 1) in Hank's solution.

So, we could conclude that all coatings are not good for real resistance applications or wear resistance enhancement. Similarly, we also found that whenever we did like titania coating, titania plus hydroxyapatite coating and titania plus zirconia oxide coating. We found that these composite coating again not so good for improving the corrosion resistance property. But again, you can understand that the titanium itself is having very good corrosion resistance when you add hydroxyapatite naturally, because of the dissolution the overall oxidation corrosion resistance property decreases.

But again, the corrosion resistance enhancement was not the main purpose of the study; main purpose of the study was to have the good fractured, highly fractured surface to fracture toughness coating. Coating with a very high fracture toughness and coating with high level of bio-active nature.

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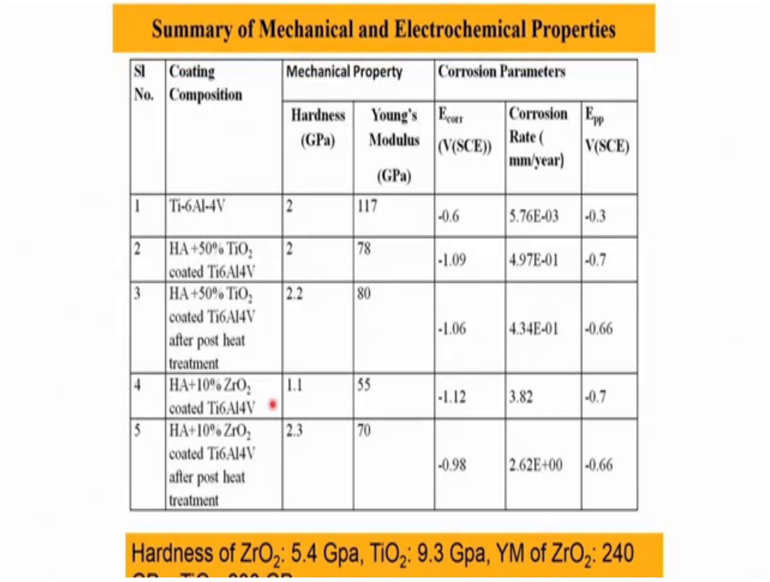

Summary of Mechanical and Electrochemical Properties

Sl No.	Coating Composition	Mechanical Property		Corrosion Parameters		
		Hardness (GPa)	Young's Modulus (GPa)	E_{corr} (V(SCE))	Corrosion Rate (mm/year)	E_{pp} V(SCE)
1	Ti-6Al-4V	2	117	-0.6	5.76E-03	-0.3
2	HA+50% TiO_2 coated Ti6Al4V	2	78	-1.09	4.97E-01	-0.7
3	HA+50% TiO_2 coated Ti6Al4V after post heat treatment	2.2	80	-1.06	4.34E-01	-0.66
4	HA+10% ZrO_2 coated Ti6Al4V	1.1	55	-1.12	3.82	-0.7
5	HA+10% ZrO_2 coated Ti6Al4V after post heat treatment	2.3	70	-0.98	2.62E+00	-0.66

Hardness of ZrO_2: 5.4 Gpa, TiO_2: 9.3 Gpa, YM of ZrO_2: 240

So finally, we just summarize the different results we found that the hardness wise the coating with the 50 percent TiO 2 and post heat treatment was having little higher hardness and what hardness enhancement was more when we added zirconia. And Young's modulus was significantly reduced and 10 percent zirconia you without heat treatment offered minimum your Young’s modulus, because for this bio-implant application we do not need very high Young's modulus.

In fact, lower the Young’s modulus better is it, closer is the Young's modulus to that of human mode better is it. So, by this particular hydroxyapatite coating in the Young's modulus was around 80 to 85 GPa so, which was reduced to 55 GPa. And if you talk about corrosion rate, again corrosion rate was reduced to a large extent not clearly to a large extent, but it was higher than that of, it was much lower than that of only hydroxyapatite based coating. And a fitting corrosion potential was also not changed to a large extent.

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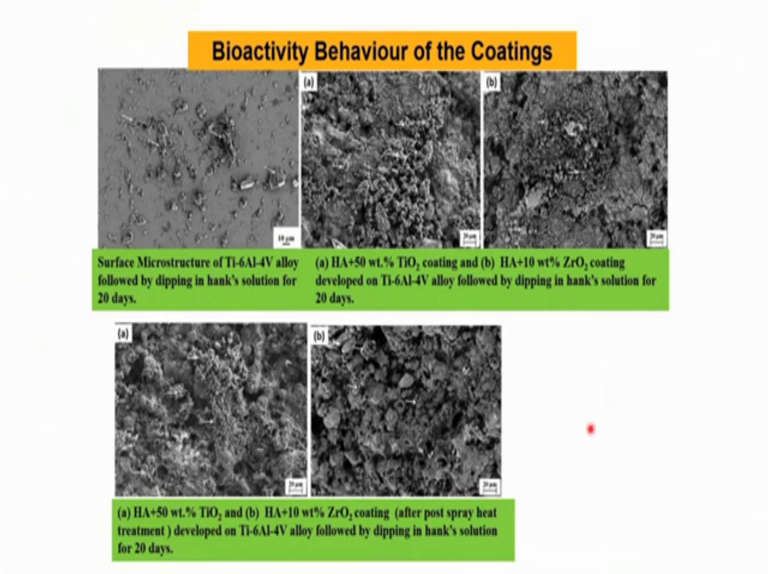

Bioactivity Behaviour of the Coatings

Surface Microstructure of Ti-6Al-4V alloy followed by dipping in hank's solution for 20 days.

(a) HA+50 wt.% TiO_2 coating and (b) HA+10 wt% ZrO_2 coating developed on Ti-6Al-4V alloy followed by dipping in hank's solution for 20 days.

(a) HA+50 wt.% TiO_2 and (b) HA+10 wt% ZrO_2 coating (after post spray heat treatment) developed on Ti-6Al-4V alloy followed by dipping in hank's solution for 20 days.

So, these kind of coating; obviously was not so beneficial in improving the corrosion resistance and wear resistance. Though under certain conditions are coating we had very good corrosion resistance as well as very good wear resistance property. But main purpose of the coating was that to increase the bio-activity and have the superior fracture toughness.

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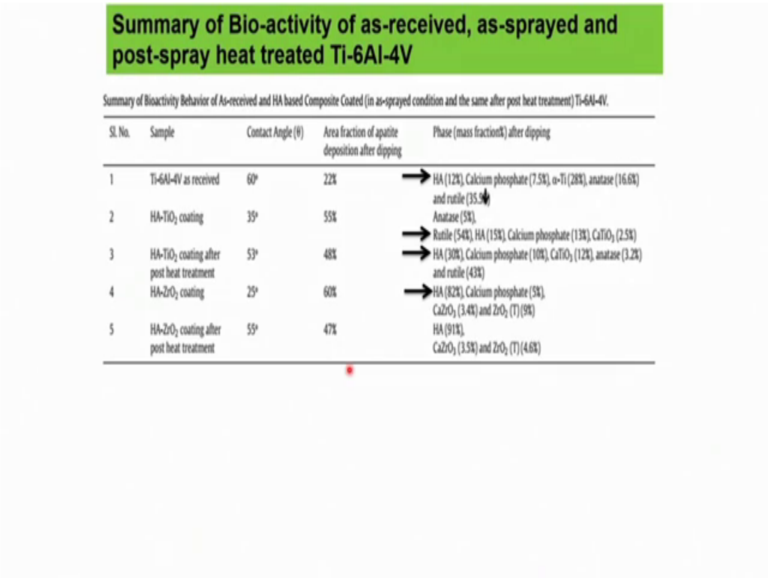

Summary of Bio-activity of as-received, as-sprayed and post-spray heat treated Ti-6Al-4V

Summary of Bioactivity Behavior of As-received and HA based Composite Coated (in as-sprayed condition and the same after post heat treatment) Ti-6Al-4V.

Sl. No.	Sample	Contact Angle (θ)	Area fraction of apatite deposition after dipping	Phase (mass fraction%) after dipping
1	Ti-6Al-4V as received	60°	22%	HA (12%), Calcium phosphate (7.5%), α-Ti (28%), anatase (16.6%) and rutile (35.9
2	HA-TiO_2 coating	35°	55%	Anatase (5%), Rutile (54%), HA (15%), Calcium phosphate (13%), $CaTiO_3$ (2.5%)
3	HA-TiO_2 coating after post heat treatment	53°	48%	HA (30%), Calcium phosphate (10%), $CaTiO_3$ (12%), anatase (3.2%) and rutile (43%)
4	HA-ZrO_2 coating	25°	60%	HA (82%), Calcium phosphate (5%), $CaZrO_3$ (3.4%) and ZrO_2 (T) (9%)
5	HA-ZrO_2 coating after post heat treatment	55°	47%	HA (91%), $CaZrO_3$ (3.5%) and ZrO_2 (T) (4.6%)

So, when we did the bio activity study, we found that bio-activity behavior was reported or maybe we analyze the bio-activity behavior of this coating by knowing the percentage of the calcium phosphate deposited when dipped in hank solution. So, we found that area fraction of appetite formation was increased by this coating, because it is quite natural because you have hydroxyapatite in the coating and that particular thing was continued.

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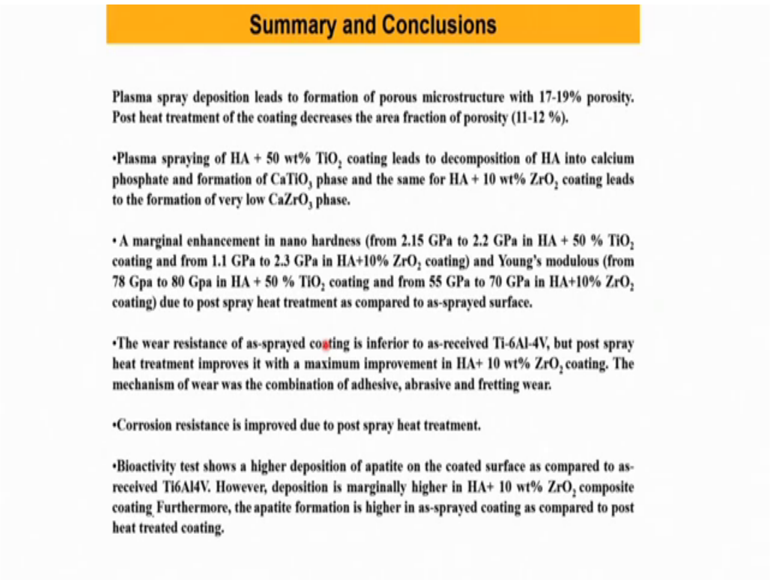

Summary and Conclusions

Plasma spray deposition leads to formation of porous microstructure with 17-19% porosity. Post heat treatment of the coating decreases the area fraction of porosity (11-12 %).

- Plasma spraying of HA + 50 wt% TiO_2 coating leads to decomposition of HA into calcium phosphate and formation of $CaTiO_3$ phase and the same for HA + 10 wt% ZrO_2 coating leads to the formation of very low $CaZrO_3$ phase.

- A marginal enhancement in nano hardness (from 2.15 GPa to 2.2 GPa in HA + 50 % TiO_2 coating and from 1.1 GPa to 2.3 GPa in HA+10% ZrO_2 coating) and Young's modulous (from 78 Gpa to 80 Gpa in HA + 50 % TiO_2 coating and from 55 GPa to 70 GPa in HA+10% ZrO_2 coating) due to post spray heat treatment as compared to as-sprayed surface.

- The wear resistance of as-sprayed coating is inferior to as-received Ti-6Al-4V, but post spray heat treatment improves it with a maximum improvement in HA+ 10 wt% ZrO_2 coating. The mechanism of wear was the combination of adhesive, abrasive and fretting wear.

- Corrosion resistance is improved due to post spray heat treatment.

- Bioactivity test shows a higher deposition of apatite on the coated surface as compared to as-received Ti6Al4V. However, deposition is marginally higher in HA+ 10 wt% ZrO_2 composite coating Furthermore, the apatite formation is higher in as-sprayed coating as compared to post heat treated coating.

And we finally, try to optimize the heat treatment parameters and have that optimum composition to be that 10 percent zirconia. After heat treatment where wear resistance was enhanced as well as the bio activity was also enhanced. But it is very much important that even though it is improved per steel where further studies are required to optimize it further. So, that we get very tough coating with the required properties as we desire.

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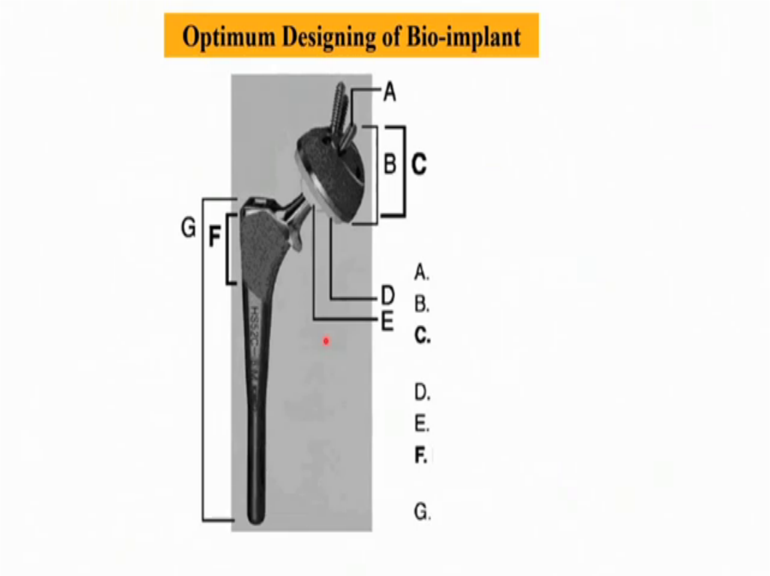

Optimum Designing of Bio-implant

So, like that this is a kind of approach which can be followed for the development of the bio active coating not only on titanium, but other materials as well and for corrosion resistance, wear resistance and also contact fatigue resistance enhancement for bio purpose. And by different studies can be conducted to know the behavior of the coating performance of the coating to a large extent.

So, whenever you deposit any layer on the surface of any substrate for a specific application, it is very important that you do characterize it properly as well as do testing in different environment to have the result and to know the performance of the coating in the given environment.

So, this is a typical of application of these particularly bioactive coating in for example, hip replacement, hip joint replacement where he found that in the steam section some part is subjected to very much in contact with human blood. So, they are the still adherence rate should be maximum. So, there if you develop this kind of coating, naturally it will promote the cell growth and naturally the implant will succeed for a long time.

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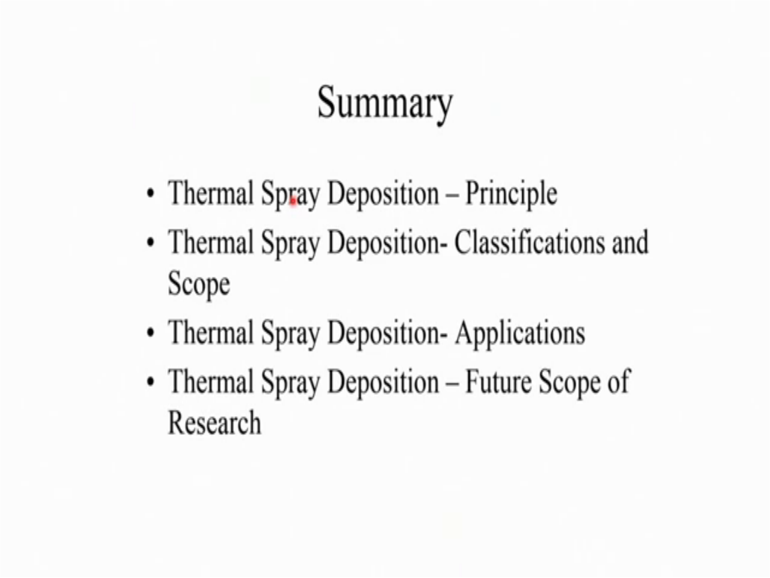

Summary

- Thermal Spray Deposition – Principle
- Thermal Spray Deposition- Classifications and Scope
- Thermal Spray Deposition- Applications
- Thermal Spray Deposition – Future Scope of Research

So finally, in summary we can say that in this particular four talks we discussed about the principle of thermal spray deposition technique, classifications and its scopes then applications. And finally, two examples of the application of the thermal spray deposition technique for a invention of newer technology or maybe in the development of newer kind of materials for different applications.

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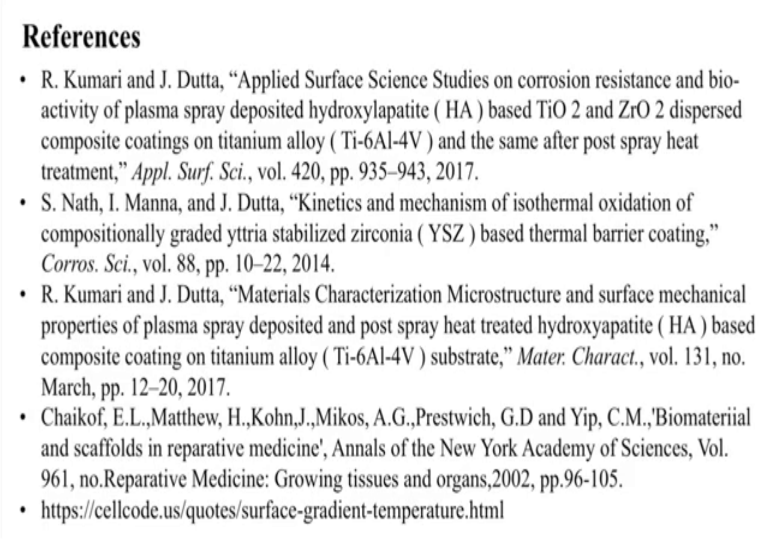

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Thank you very much.