

**Metal Additive Manufacturing**  
**Prof. Janakranjan Ramkumar**  
**Prof. Amandeep Singh Oberoi**  
**Department of Mechanical Engineering and Design**  
**Indian Institute of Technology, Kanpur**  
**Lecture 27**

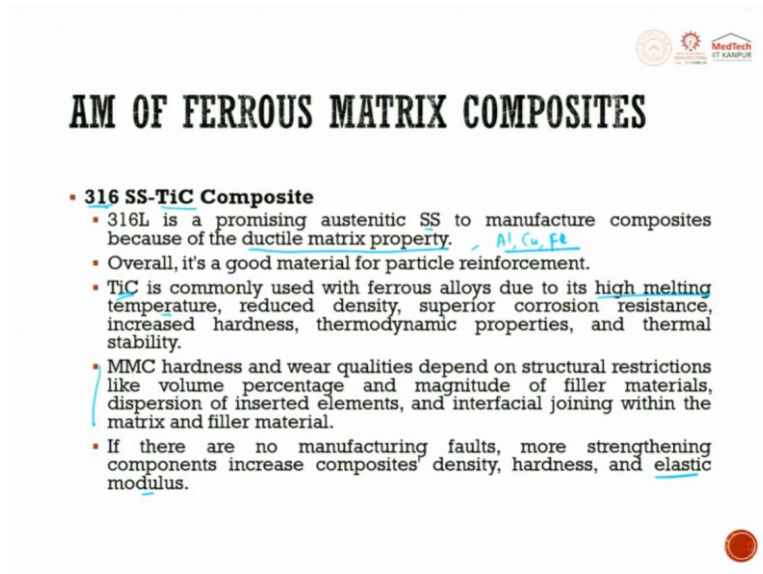
**Additive Manufacturing of Metal Matrix Composites (Part 2 of 4)**

(Refer Slide Time: 00:19)



In continuing with the previous lecture on metal matrix composites manufactured through additive manufacturing. So, we are now going to look into different types of matrix, how are these matrix formed using additive manufacturing, matrix and composite formed using additive manufacturing. So, we have ferrous matrix, we have titanium matrix.

(Refer Slide Time: 00:44)



## AM OF FERROUS MATRIX COMPOSITES

- **316 SS-TiC Composite**
  - 316L is a promising austenitic SS to manufacture composites because of the ductile matrix property. *Al, Cu, Fe*
  - Overall, it's a good material for particle reinforcement.
  - TiC is commonly used with ferrous alloys due to its high melting temperature, reduced density, superior corrosion resistance, increased hardness, thermodynamic properties, and thermal stability.
  - MMC hardness and wear qualities depend on structural restrictions like volume percentage and magnitude of filler materials, dispersion of inserted elements, and interfacial joining within the matrix and filler material.
  - If there are no manufacturing faults, more strengthening components increase composites' density, hardness, and elastic modulus.

So, when we talk about ferrous, people very commonly use 316, SS 316, if you talk about food processing they talk about SS 316, they talk about varying application, heavy industries, SS 316 is very commonly used. Now using this SS 316 and reinforcing with TiC to form a metal matrix composite will be our discussion. 316L is a promising austenitic SS to manufacture component because of the ductile matrix property.

If you have brittle matrix property, then adding this reinforcement is not going to take us anywhere. So, it is always a good idea to choose a matrix which has ductility. Overall, it is a good material for particle reinforcement. So, this ductile matrix is very good so, that is why we always prefer if you see Al, copper then we used to do aluminium, then we used to do iron, all these fellows are having ductility inbuilt in their material. So, overall it is a good material for particle reinforcement.

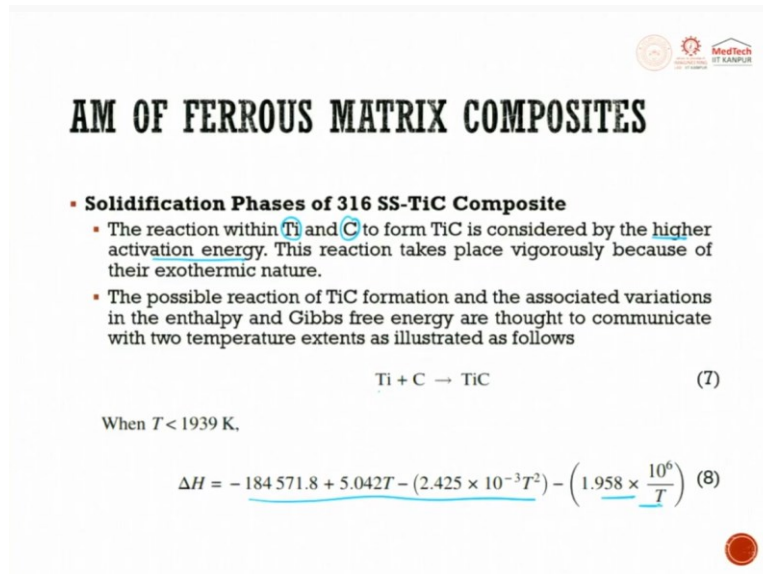
TiC is commonly used with ferrous alloys due to its high melting temperature. TiC has high melting temperature, then reduced density, superior corrosion resistance, increase the hardness, thermodynamic properties and thermal stability. So, all these things are there when TiC is added to ferrous alloys, it tries to have improve or increase the melting point then reduce the density so that it can float or some application, then superior corrosion resistance because T will always have a problem of corrosion, increased hardness, then thermodynamic property while conducting and other things and thermal stability.

Metal matrix composite hardness and wear qualities depend on structural restriction like volume percentage and magnitude of filler material, dispersion of inserted elements and interfacial joining with the matrix and filler material. So, this all is going to be the advantage

which metal matrix has, if there are no manufacturing fault, more strengthening component increase composites density, hardness and elastic modulus.

So, this is also part of the metal matrix composite which is made through additive manufacturing, there is a big difference in the properties of additive manufacture, because, here it undergoes the acquainting cycle grain requirement. So, you will get a better property response compared to that.

(Refer Slide Time: 03:47)



**AM OF FERROUS MATRIX COMPOSITES**

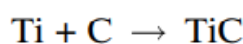
- **Solidification Phases of 316 SS-TiC Composite**
  - The reaction within Ti and C to form TiC is considered by the higher activation energy. This reaction takes place vigorously because of their exothermic nature.
  - The possible reaction of TiC formation and the associated variations in the enthalpy and Gibbs free energy are thought to communicate with two temperature extents as illustrated as follows

$$\text{Ti} + \text{C} \rightarrow \text{TiC} \quad (7)$$

When  $T < 1939 \text{ K}$ ,

$$\Delta H = -184571.8 + 5.042T - (2.425 \times 10^{-3}T^2) - \left(1.958 \times \frac{10^6}{T}\right) \quad (8)$$

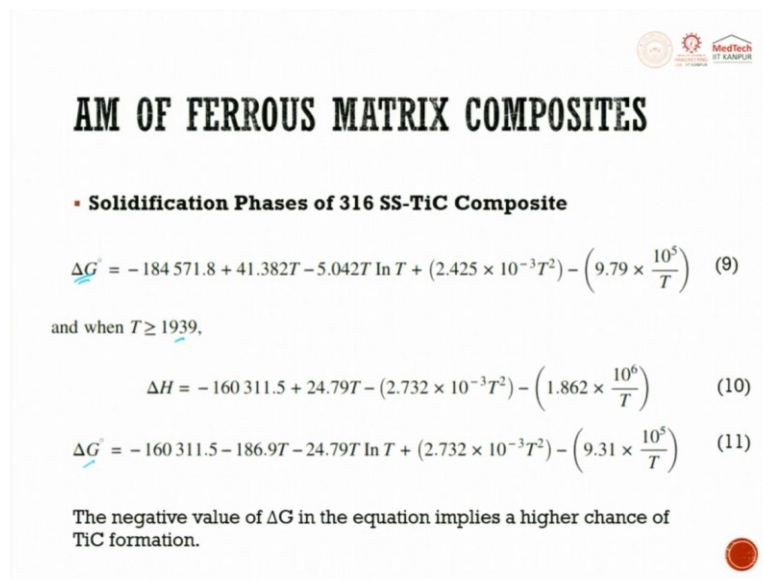
The solidification phase of 316 SS TiC composite, the reaction within Ti and C to form TiC is considered by the higher activation energy. First, we are trying to mix Ti and C. So, that is because of the higher activation energy. This reaction takes place vigorously because of their exothermic nature. Ti and C because of the high activation energy they try to mix and they form a TiC and which is a stable phase. The possible reaction of TiC formation and the associated variations in the enthalpy and the Gibbs free energy are thought to communicate with two temperature extend as illustrated below.



When  $T < 1939 \text{ K}$ ,

$$\Delta H = -184571.8 + 5.042T - (2.425 \times 10^{-3}T^2) - \left(1.958 \times \frac{10^6}{T}\right)$$

(Refer Slide Time: 04:52)



**AM OF FERROUS MATRIX COMPOSITES**

▪ **Solidification Phases of 316 SS-TiC Composite**

$$\Delta G^\circ = -184\,571.8 + 41.382T - 5.042T \ln T + (2.425 \times 10^{-3}T^2) - \left(9.79 \times \frac{10^5}{T}\right) \quad (9)$$

and when  $T \geq 1939$ ,

$$\Delta H = -160\,311.5 + 24.79T - (2.732 \times 10^{-3}T^2) - \left(1.862 \times \frac{10^6}{T}\right) \quad (10)$$
$$\Delta G^\circ = -160\,311.5 - 186.9T - 24.79T \ln T + (2.732 \times 10^{-3}T^2) - \left(9.31 \times \frac{10^5}{T}\right) \quad (11)$$

The negative value of  $\Delta G$  in the equation implies a higher chance of TiC formation.

So, delta G is the Gibbs free energy which is written again in this form.

$$\Delta G^\circ = -184\,571.8 + 41.382T - 5.042T \ln T + (2.425 \times 10^{-3}T^2) - \left(9.79 \times \frac{10^5}{T}\right)$$

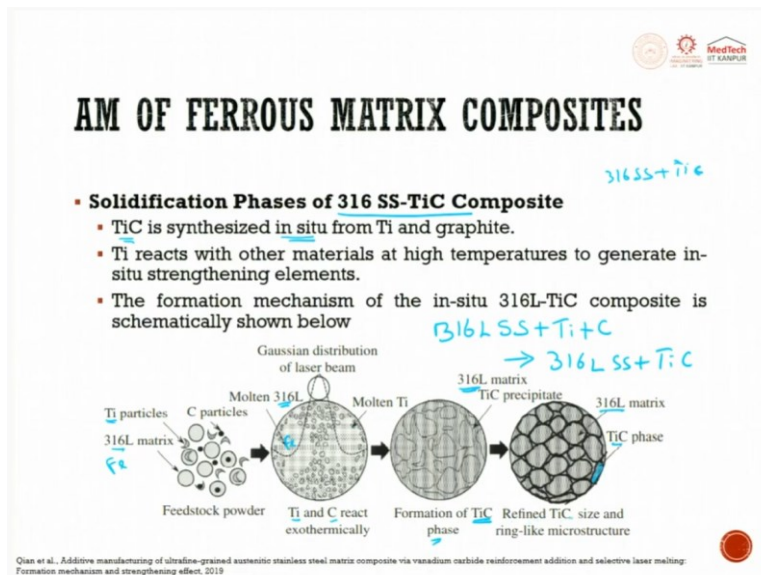
and when  $T \geq 1939$ ,

$$\Delta H = -160\,311.5 + 24.79T - (2.732 \times 10^{-3}T^2) - \left(1.862 \times \frac{10^6}{T}\right)$$

$$\Delta G^\circ = -160\,311.5 - 186.9T - 24.79T \ln T + (2.732 \times 10^{-3}T^2) - \left(9.31 \times \frac{10^5}{T}\right)$$

And when T is greater than or equal to 1939 you can see that  $\Delta H$  enthalpy and Gibbs free energy written. The negative value of  $\Delta G$  in the equation implies a higher chance of TiC formation.

(Refer Slide Time: 05:15)



In the solidification phase of 316 SS TiC composite, TiC is synthesised in situ, from Ti and graphite. Ti reacts with the other material at high temperatures to generate in situ strengthening elements. So, TiC they do a in situ. In-situ means during the reaction it forms. The formation mechanism of this in situ, TiC composite is schematically shown below. So, you have a Gaussian distribution of laser beam hitting at a surface. So, this is the feedstock powder wherein which you have these are all 316 matrix which is basically iron, and then you have Ti particle which is mixed and you have graphite which is added.

So, now you see there, all the 316 matrix, Ti particles, C particles, they inturn react very fastly to form TiC. And this TiC will be a particulate reinforcement in the matrix 316. So, when you look at this exothermic reaction which happens here, when the laser hits, it has a peak power coming here. So, here the laser hits, then Ti and C reacts to form TiC and this TiC is getting dispersed in the FE matrix.

So, you can see molten, these are all molten 316L which is basically iron, stainless steel which is iron. So, here what will happen is you can see molten Ti are here and you also have carbon. So, now this gets transformed with the formation of TiC phases, so these are all TiC precipitation which is there in 316L matrix. So, now, this gets further refined, TiC sized and ring like microstructure, you will see here 316L matrix and TiC phase which are getting formed, these are all TiC phase.

So, now you can visualise how easily all these things happen by exposing it to a laser and trying to have it in one layer. So initially it is 316L SS +Ti +C giving you 316L which is the matrix SS +TiC. So, you can see exothermic reaction happening then you will see a formation of TiC which happens, which are precipitated along the grain boundary and then

you will try to see refinement of TiC sized and ring like microstructure. You see all the things which are there.

So, now it is very clear, how do we form this composite in powder metallurgy route. Many a times what people do is they try to have 316 SS+TiC direct they take. So, it can be like this or it can be like this. Here, we can use selective laser sintering process or selective laser melting. So, if you see that grain refinement happening, refined TiC size and ring like microstructure gives you a performance such that they can have very high properties whatever you want.

(Refer Slide Time: 08:50)

The slide is titled "AM OF FERROUS MATRIX COMPOSITES" in bold black text. Above the title, a handwritten blue arrow points to the text "Selectively reinforcement composite". To the right of the title, there are logos for "Mediatech" and "IIT KANPUR". Below the title, there is a list of six bullet points. To the right of the list, there is a handwritten blue diagram of a square with a diagonal line, labeled "TiC rich" and "TiC lean".

**AM OF FERROUS MATRIX COMPOSITES**

- TiC reinforcements are found at grain boundaries and inside columnar dendrites in laser-based AM procedures.
- Higher solidification rates segregate TiC elements, causing this.
- Strong chaotic fluxes in liquid melt intensify heavy particles in surrounding turbulences.
- Chemical inhomogeneity can affect the concentration contour, and structural supercooling can affect the solidification approach and volume of TiC precipitates.
- Small contact time and fast heat transfer can reduce TiC precipitates.
- Multiple laser scans over previously melted layers can increase TiC volume due to accumulated heat.

Handwritten notes and diagram: "Selectively reinforcement composite", "TiC rich", "TiC lean".

The TiC reinforcement are found at grain boundaries refining along precipitate, right. TiC reinforcement are found at the grain boundaries and inside the columnar dendrites in laser based additive manufacturing. So, columnar dendrites, these are dendritic structures, which are formed, these are dendritic structures, these dendritic structures go and in between, maybe TiC will be formed.

Higher solidification rates segregates TiC elements causing this. Strong chaotic fluxes in liquid melt intensify heavy particles in the surrounding turbulence. Chemical inhomogeneity can affect the concentration contour and structural super cooling can affect the solidification approach and volume of TiC precipitate. The chemical inhomogeneity can affect the concentration contour and structural super cooling.

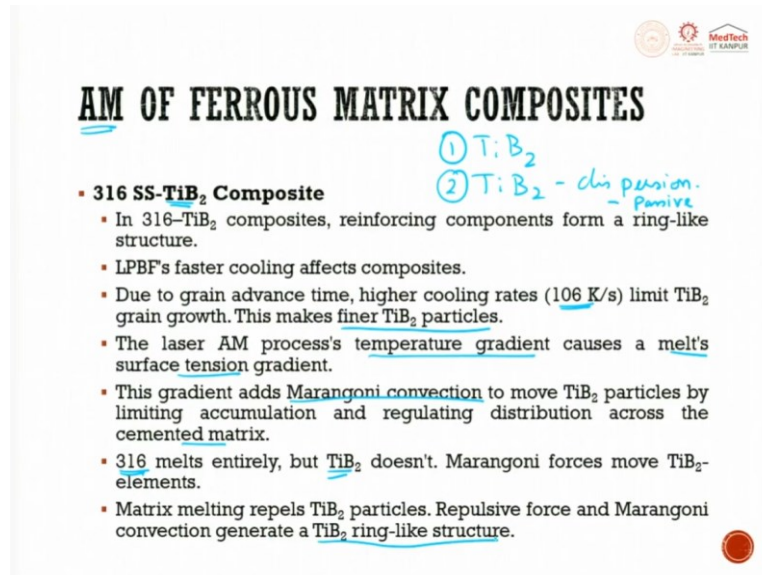
What is super cooling? We saw super cooling in solidification, can affect the solidification approach and volume of TiC precipitate. So, the volume of TiC forming also can be played very nicely by choosing the parameters. So, the chemical inhomogeneity can affect the concentration contour. Small contact time and fast heat transfer can reduce TiC precipitation, when the laser is moving very fast and if the laser is taken to a very high temperature, then what will happen is you will have reduced TiC precipitation formation.

Multiple laser scans over previously melted layer can increase TiC volume due to accumulated heat. So, you play with the heat parameters which comes into the process and you try to see how is TiC getting formed. How is TiC quantum could be changed easily. So, what does it mean? This tries to give me selectively reinforced composites.



So, what does it mean is, I can selectively tune to increase in one zone for example, if you have a zone of a composite like this, this zone you can have TiC rich, this zone you can try to have TiC lean and in between you can have a moderate region. So now you are able to play with this property, since it is additive to manufacturing use.

(Refer Slide Time: 11:53)



**AM OF FERROUS MATRIX COMPOSITES**

①  $TiB_2$   
②  $TiB_2$  - dispersion. Passive

- **316 SS- $TiB_2$  Composite**
  - In 316- $TiB_2$  composites, reinforcing components form a ring-like structure.
  - LPBF's faster cooling affects composites.
  - Due to grain advance time, higher cooling rates (106 K/s) limit  $TiB_2$  grain growth. This makes finer  $TiB_2$  particles.
  - The laser AM process's temperature gradient causes a melt's surface tension gradient.
  - This gradient adds Marangoni convection to move  $TiB_2$  particles by limiting accumulation and regulating distribution across the cemented matrix.
  - 316 melts entirely, but  $TiB_2$  doesn't. Marangoni forces move  $TiB_2$  elements.
  - Matrix melting repels  $TiB_2$  particles. Repulsive force and Marangoni convection generate a  $TiB_2$  ring-like structure.

The 316  $TiB_2$  I am now changing TiC with  $TiB_2$ , titanium boride. So, that was titanium carbide. So, titanium boride composite reinforcing components form a ring like structure. Generally, we try to use laser powder bed fusion method which faster cooling affects the composite. Due to grain advance time, higher cooling rate which goes up 106 K/s limit TiB to grain growth. This makes finer  $TiB_2$  particle.

If you want to make finer  $TiB_2$  particle, this is one of the easiest and the fastest way of making it. Today there is a lot of research going in the area of additive manufacturing and metal matrix composites. The laser additive manufacturing process temperature gradient causes a melt surface tension gradients. This gradient adds Marangoni convection to move  $TiB_2$  particles by limiting accumulation and the regulating distribution across the cemented matrix.

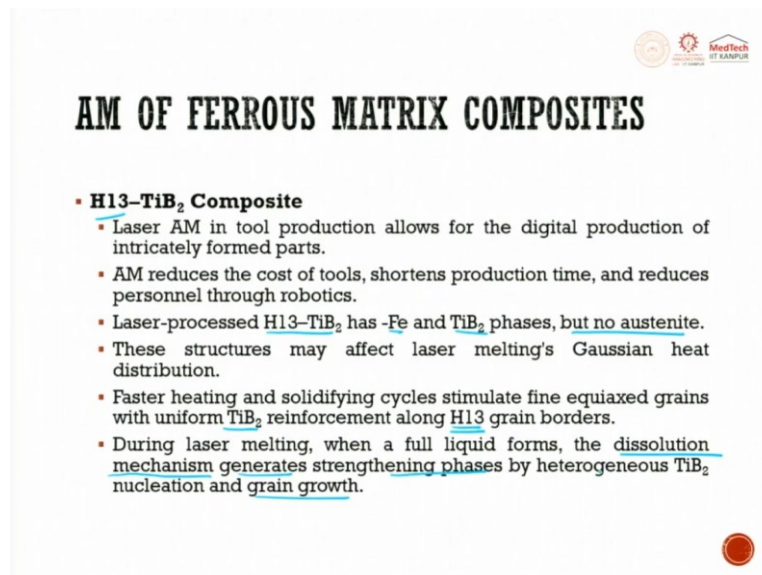
So, what is the other thing you have to do? See, first is  $TiB_2$ , next is  $TiB_2$  dispersion. This dispersion should be done in a passive manner that means to say so, the process itself tries to bring in that dispersion. So that is what we are doing. How will the process itself because of the Marangoni convection effect, this gradient, what is the gradient, the temperature gradient.



The temperature gradient adds to Marangoni convection to move the  $\text{TiB}_2$  particles by limiting accumulation and regulating distribution across the cemented matrix. 316 melts entirely, but  $\text{TiB}_2$  does not, this melt, this does not. So, Marangoni forces move the  $\text{TiB}_2$  elements. So, it pushes it when the liquid, it assumes that there is a river which is flowing and a boat which is there. So, the river when it moves, the boat which is there that also moves. So that is what is Marangoni forces  $\text{TiB}_2$  elements.

Matrix melting ripples  $\text{TiB}_2$  particles, repulsive force and Marangoni convection generate a  $\text{TiB}_2$  ring like structure. The same  $\text{TiC}$  ring like we also have  $\text{TiB}_2$  ring like structure. Same thing.

(Refer Slide Time: 14:25)



The slide is titled "AM OF FERROUS MATRIX COMPOSITES" in bold black text. It features a bulleted list of points about the H13-TiB<sub>2</sub> composite. The list includes details about laser AM in tool production, cost reduction, production time, personnel reduction, and the microstructure of the composite. The slide also has logos for MedTech and IIT Kanpur in the top right corner and a red circular logo in the bottom right corner.


- **H13-TiB<sub>2</sub> Composite**
  - Laser AM in tool production allows for the digital production of intricately formed parts.
  - AM reduces the cost of tools, shortens production time, and reduces personnel through robotics.
  - Laser-processed H13-TiB<sub>2</sub> has -Fe and TiB<sub>2</sub> phases, but no austenite.
  - These structures may affect laser melting's Gaussian heat distribution.
  - Faster heating and solidifying cycles stimulate fine equiaxed grains with uniform TiB<sub>2</sub> reinforcement along H13 grain borders.
  - During laser melting, when a full liquid forms, the dissolution mechanism generates strengthening phases by heterogeneous TiB<sub>2</sub> nucleation and grain growth.

So now let us see the third variant of additive manufactured ferrous matrix composite, H13  $\text{TiB}_2$ . So, H13 is exhaustively used for heavy industries application. So, here laser additive manufacturing in tool production allows for the digital production of intricately formed parts. AM reduces the cost of tools, shortens the production time and reduces the personnel through robotics.

Laser process H13  $\text{TiB}_2$  has Fe and  $\text{TiB}_2$  phase, but no austenite phase. These structures may affect laser melting Gaussian heat distribution. Faster heating and solidifying cycle stimulate fine equiaxed grains with uniform  $\text{TiB}_2$  reinforcement along H13 grain boundary. During laser melting, when a full liquid forms, the dissolution mechanism generates strengthening phases by heterogeneous  $\text{TiB}_2$  nucleation and grain growth. Its all very nicely written, dissolution mechanism generate strengthening so, dissolution is what, you try to diffuse material into the matrix. So, this will try to strengthen phase by heterogeneous  $\text{TiB}_2$ .




(Refer Slide Time: 16:03)



## AM OF FERROUS MATRIX COMPOSITES

- **H13-TiC Composite**
  - The laser's faster heating and cooling cycle helps TiC structures happen by shortening the amount of time TiC grains need to grow.
  - When the temperature goes up, the Marangoni flow gets stronger, and capillary forces push the liquid along.
  - So, the shear and rotational forces that form around the TiC particles could be a driving force for the particles to spread out evenly, which stops them from sticking together.
  - Also, when the volumetric energy density is lower, the torque is less, which makes particles stick together more.



So you also have H13 TiC almost the same thing. The laser, faster heating and cooling cycle helps TiC structures happen by shortening the amount of time TiC grains need to grow. So, TiC grains need to grow. So, we saw that TiC grain growth in this graph, refinement of TiC size and ring like microstructure we saw almost the same thing is also common here. So, the laser, faster heating and cooling cycle helps TiC structures happen by shortening the amount of time TiC grains needs to grow.

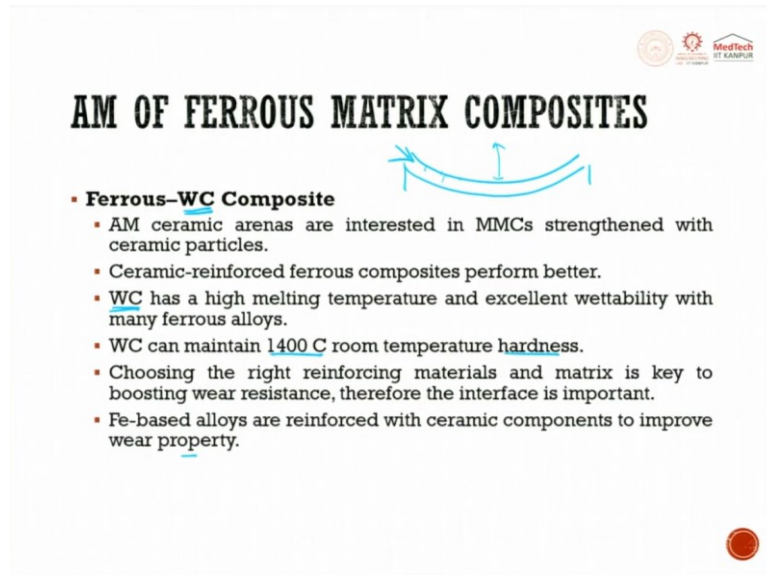
When the temperature goes up, the Marangoni flow gets stronger. When the Marangoni gets stronger, what happens, it tries to have lots of vortex. So it tries to have more turbulent action and capillary force pulls the liquid along. Movement can happen, Marangoni flow. The capillary force pushes the liquid along. So now there has to be boats and these two will try to disperse TiC give you well dispersed H13 metal matrix composite.

So, the shear and rotational forces, the rotation is through Marangoni capillary shear. So, the shear and rotational force that form around the TiC particles could be a driving force for the particles to spread out evenly, which stops them from sticking together. So, there will be a shearing and a rotational force that forms around the TiC. So, TiC particle is here. This is TiC and then there will be a shear and the driving rotational force could be a driving force, TiC particles could be a driving force for the particles to spread out evenly, which stops them from sticking together.

So, this motion of Marangoni force and capillary action tries to disperse TiC particles nicely in H13 matrix. I said passive dispersion is the best way. If you can disperse these reinforcing particles without applying a shearing action, then they easily disperse. If you do a shearing

action the mechanical force many a times does not give uniform dispersion. So here this shear rotation for gives you that. Also, when the volumetric energy density is lower, the torque is less, which makes particles stick together more. So, we try to have a trade off and try to disperse the TiC particles in H13 matrix.

(Refer Slide Time: 18:57)



The slide is titled "AM OF FERROUS MATRIX COMPOSITES" in bold, black, serif font. Above the title is a diagram of a curved beam with two upward-pointing arrows indicating forces. To the right of the title are three logos: a circular one, a gear-like one, and one for "MedTech". Below the title is a bulleted list of points. The first point is "Ferrous-WC Composite". The subsequent points are: "AM ceramic arenas are interested in MMCs strengthened with ceramic particles.", "Ceramic-reinforced ferrous composites perform better.", "WC has a high melting temperature and excellent wettability with many ferrous alloys.", "WC can maintain 1400 C room temperature hardness.", "Choosing the right reinforcing materials and matrix is key to boosting wear resistance, therefore the interface is important.", and "Fe-based alloys are reinforced with ceramic components to improve wear property." A small red circular logo is in the bottom right corner of the slide.

## AM OF FERROUS MATRIX COMPOSITES

- **Ferrous-WC Composite**
  - AM ceramic arenas are interested in MMCs strengthened with ceramic particles.
  - Ceramic-reinforced ferrous composites perform better.
  - WC has a high melting temperature and excellent wettability with many ferrous alloys.
  - WC can maintain 1400 C room temperature hardness.
  - Choosing the right reinforcing materials and matrix is key to boosting wear resistance, therefore the interface is important.
  - Fe-based alloys are reinforced with ceramic components to improve wear property.

The last one in the ferrous is going to be with respect to tungsten carbide. Tungsten carbide are heavy and they are used for wear resistance property and hardness enhancing property. So additive manufacturing ceramic arenas are interested in metal matrix composites strengthened with ceramic particles. Ceramic reinforcements ferrous composite, perform much better.


Tungsten carbide are high melting temperature and excellent wettability with many ferrous alloys. Why are we talking about it? Whenever you have an application for example, you have an iron cable, through this iron cable there is current which is moving. So now when we try to add these reinforcing agents, it can be carbon graphite, graphene and other things, if you try to add them along with this tungsten carbide, it will try to avoid sagging.

So, moment sagging is reduced so then what happens? The number of posts which are used for reinforcements can be reduced. So, here what happens they always look for high melting temperature such that the deflection cannot happen so easily. High melting temperature and excellent wettability with many ferrous alloys are done by using this tungsten carbide.

Tungsten Carbide can maintain 1400<sup>0</sup> C room temperature hardness. Look at the amount of temperature rise it can give and maintain the hardness. Choosing the right reinforcing materials and matrix is the key boosting wear resistance and therefore, the interface is

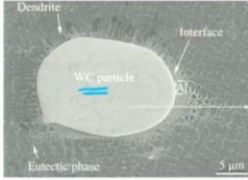
important. Iron based alloys are reinforced with ceramic components to improve their wear properties.

(Refer Slide Time: 20:55)



## AM OF FERROUS MATRIX COMPOSITES

- **Ferrous-WC Composite**
  - In Fe-WC composite, dissolved WC reinforcing components release W and C in the liquid melt.
  - W and C atoms react with ferrous alloy to generate carbides near grain boundaries.
  - The gradient interface MC<sub>3</sub> (M = W, Fe, Cr, Ni) develops between WC reinforcing element and matrix during laser AM procedures.
  - Gradient interfaces may strengthen WC and Fe matrix bonds.
  - Size and shape of the interface gradient fluctuate with laser power, intensity, and spot size.



Microstructure showing the morphology of matrix, interface, and WC reinforcement in MMC.

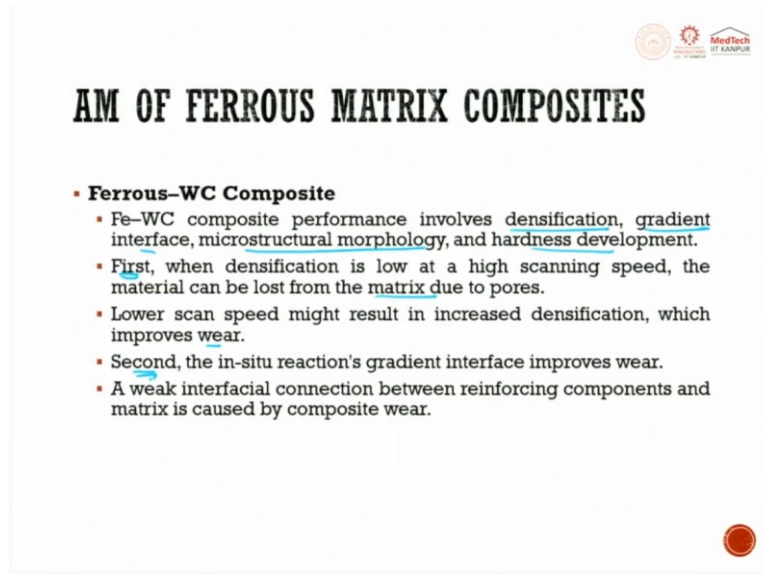
Gu et al. Laser additive manufactured WC reinforced Fe-based composites with gradient reinforcement/matrix interface and enhanced performance. Compos. Struct. 2018

So, this is the tungsten carbide particle. This is the dendritic growth which happens, this is an interface which we already discussed and this is the eutectic phase of iron which is there. This is a microstructure which shows the morphology of matrix and matrix interface and tungsten carbide reinforcement.

The iron tungsten carbide composites dissolved tungsten carbide reinforcing component releases tungsten and carbon in the liquid metal. Tungsten and carbon atoms react with alloys to generate carbides near the grain boundary. The gradient interface MC<sub>3</sub>, M is tungsten, M can be tungsten, M can be iron, M can be chromium, M can be nickel, it develops between tungsten carbide reinforcing element and the matrix during the laser additive manufacturing. It gives you a new completely new component, new intermetallics, all these things are formed in this additive manufactured route.

Gradient interface may strengthen tungsten carbide and Fe matrix bonds, size and shape of the interface gradient fluctuates with laser power, intensity and spot size. So, this is very, very interesting phenomena. And here you can see it tries to form gradients interface.

(Refer Slide Time: 22:25)



The slide is titled "AM OF FERROUS MATRIX COMPOSITES" in a bold, black, serif font. In the top right corner, there are three logos: a circular logo with a gear, a red logo with a gear, and a logo for "MedTech IIT KANPUR". The main content is a bulleted list under the heading "Ferrous-WC Composite". The list contains five points, each starting with a red square bullet. The text is in a black, sans-serif font. A small red circular logo is in the bottom right corner of the slide.

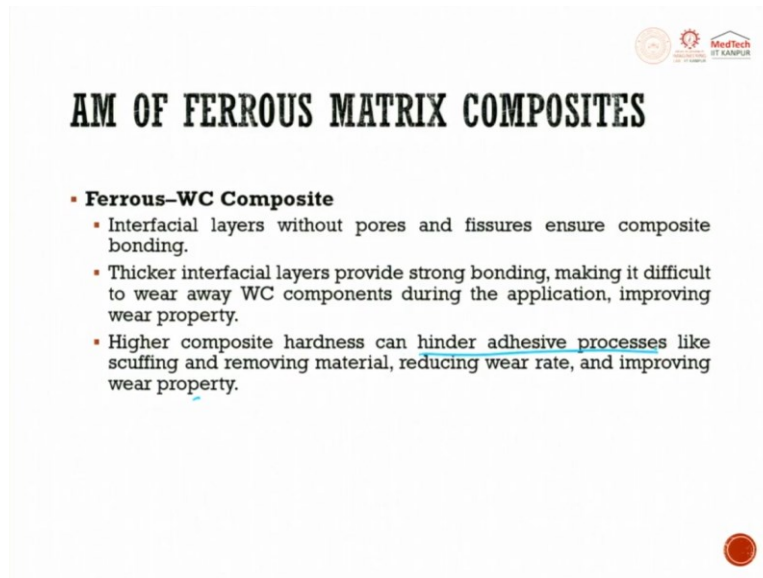
## AM OF FERROUS MATRIX COMPOSITES

- **Ferrous-WC Composite**
  - Fe-WC composite performance involves densification, gradient interface, microstructural morphology, and hardness development.
  - First, when densification is low at a high scanning speed, the material can be lost from the matrix due to pores.
  - Lower scan speed might result in increased densification, which improves wear.
  - Second, the in-situ reaction's gradient interface improves wear.
  - A weak interfacial connection between reinforcing components and matrix is caused by composite wear.

Iron tungsten carbide composite performance involves densification, gradient interface, microstructural morphology and hardness development. All these things are possible by using this Fe tungsten carbide densification, gradient interface, microstructure morphology and hardness development.

First when densification is low at high scanning speeds, the material can be lost from the matrix due to pores. When you try to do with low scan speed might result in increase in densification which improves wear resistance. Second, the in situ reaction's gradient, interface improves wear. The weak interfacial connection between the reinforcing component and the matrix is caused by composite wear. So that is first and second. So, we have to go through it nicely to get to the output.

(Refer Slide Time: 23:24)



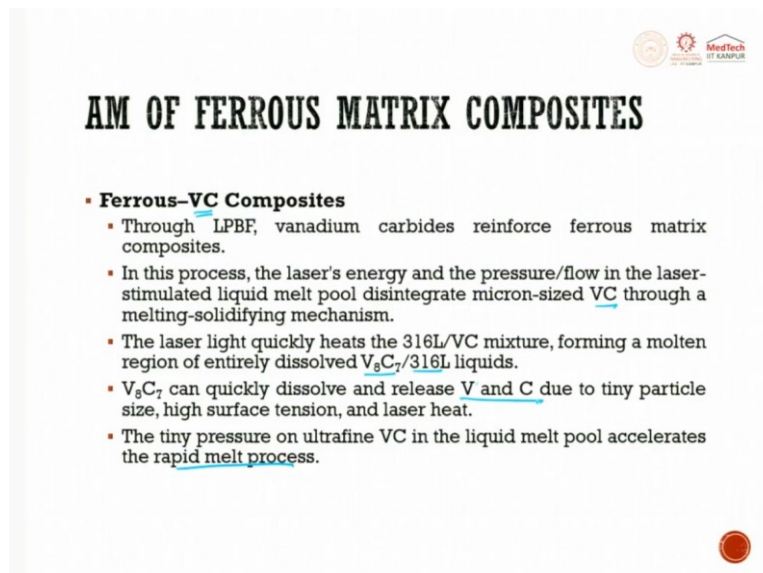
The slide is titled "AM OF FERROUS MATRIX COMPOSITES" in a bold, black, serif font. In the top right corner, there are three logos: a circular logo with a gear, a red gear logo, and the "MedTech IIT KANPUR" logo. The main content is a bulleted list under the heading "Ferrous-WC Composite". The list includes three points: interfacial layers ensuring bonding, thicker layers improving wear resistance, and higher hardness hindering adhesive processes. A small red circular logo is in the bottom right corner.

## AM OF FERROUS MATRIX COMPOSITES

- **Ferrous-WC Composite**
  - Interfacial layers without pores and fissures ensure composite bonding.
  - Thicker interfacial layers provide strong bonding, making it difficult to wear away WC components during the application, improving wear property.
  - Higher composite hardness can hinder adhesive processes like scuffing and removing material, reducing wear rate, and improving wear property.

The interfacial layers without porous and fissures ensures composite bonding. Thicker interface layer provide stronger bonding, making it difficult to wear away tungsten carbide components during the application improving wear resistance property. The higher composite hardness can hinder adhesive process like scuffing and removing material reducing wear rate and improving wear property. So, these are something which is important like higher composite hardness can hinder the adhesive processes.

(Refer Slide Time: 24:03)



The slide is titled "AM OF FERROUS MATRIX COMPOSITES" in a bold, black, serif font. In the top right corner, there are three logos: a circular logo with a gear, a red gear logo, and the "MedTech IIT KANPUR" logo. The main content is a bulleted list under the heading "Ferrous-VC Composites". The list includes five points: LPBF process, laser-stimulated liquid melt pool disintegration, laser heating of 316L/VC mixture, dissolution of V<sub>8</sub>C<sub>7</sub>, and acceleration of rapid melt process by tiny pressure. A small red circular logo is in the bottom right corner.

## AM OF FERROUS MATRIX COMPOSITES

- **Ferrous-VC Composites**
  - Through LPBF, vanadium carbides reinforce ferrous matrix composites.
  - In this process, the laser's energy and the pressure/flow in the laser-stimulated liquid melt pool disintegrate micron-sized VC through a melting-solidifying mechanism.
  - The laser light quickly heats the 316L/VC mixture, forming a molten region of entirely dissolved V<sub>8</sub>C<sub>7</sub>/316L liquids.
  - V<sub>8</sub>C<sub>7</sub> can quickly dissolve and release V and C due to tiny particle size, high surface tension, and laser heat.
  - The tiny pressure on ultrafine VC in the liquid melt pool accelerates the rapid melt process.

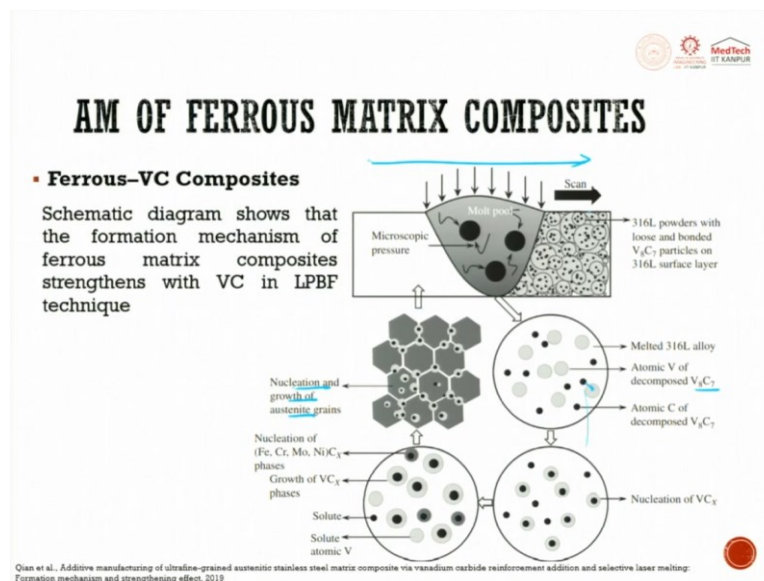
We can also have vanadium carbide through laser powder bed fusion, vanadium carbide reinforcements ferrous matrix composite is also thought of. In this process, the laser energy



and the measure per flow in the laser, stimulated liquid metal pool disintegrate micron sized vanadium carbide through a melting solidifying mechanism.

The laser light quickly heats the 316L vanadium carbide mixture, forming a molten region entirely dissolved vanadium carbide and 316L liquid. The vanadium carbide can quickly dissolve and release vanadium and carbon due to tiny particle size, high surface tension and laser heat. The tiny pressure of ultra fine VC in the liquid melt pool accelerates the rapid melting process. It is very nicely process happens. So, how is V3 or V8 C7 can quickly dissolve and release V and C separately.

(Refer Slide Time: 25:13)



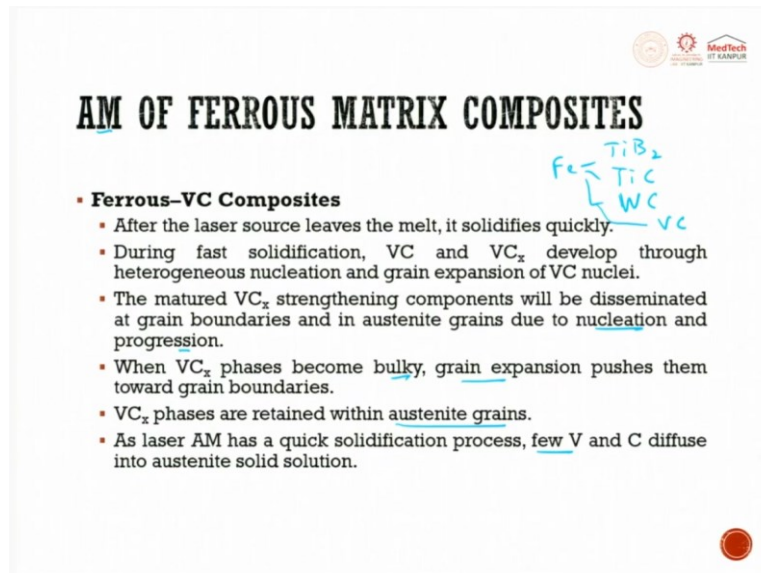
Ferrous vanadium carbide composite, the schematic diagram shows the formation of mechanism of ferrous matrix composite strengthening with VC in laser powder bed fusion method. So, you have part. So, in this you see there the scanning is moving from this place to this place. So, these are all fresh powder where still the laser has not come in contact. If you look at this very nicely it has 316L powder with loose and bonded  $V_8C_7$  particles of 316L surface layer.

So, this when it is initially like this, you will have, when the laser hits you will have melted 316L alloy, then you will have atomic V of decomposed  $V_8C_7$  and you will have atomic C which is decomposed again from  $V_8C_7$ . So, here by laser these are getting split. Now, these nucleation of  $VC_x$  happens. These are nucleation which happens so, this gets diffused and other things.

So, now from here you can see here it tries to nucleate of iron or chromium on molybdenum nickel carbide phase the growth of  $VC_x$  phase, you will have a solute and then you will have a solute atom of V. From here what happened, the nucleation grows, and you have a nucleation and growth of austenite grain. So, the cycle goes very interestingly like this. So, whatever  $V_8C$  was there it splits then the splitting happens.

Now this splitting happens, you will have C separately, V separately. This V wherever it is that the C tries to diffuse inside and forms a  $VC_x$ . Now, this  $VC_x$  then what happens, it tries to form a nucleation in the matrix. So, you will try to have nuclear Fe chromium molybdenum nickel phase with a growth and then parallelly what happens this VC which is there which tries to grow. So, then this will be the final nucleation and growth of the austenite phase.

(Refer Slide Time: 27:13)



**AM OF FERROUS MATRIX COMPOSITES**

**Ferrous-VC Composites**

- After the laser source leaves the melt, it solidifies quickly.
- During fast solidification, VC and  $VC_x$  develop through heterogeneous nucleation and grain expansion of VC nuclei.
- The matured  $VC_x$  strengthening components will be disseminated at grain boundaries and in austenite grains due to nucleation and progression.
- When  $VC_x$  phases become bulky, grain expansion pushes them toward grain boundaries.
- $VC_x$  phases are retained within austenite grains.
- As laser AM has a quick solidification process, few V and C diffuse into austenite solid solution.

Handwritten diagram:  $TiB_2$  at the top, with arrows pointing down to  $Fe$ ,  $TiC$ , and  $WC$ . A bracket on the right side of these three points down to  $VC$ .

After the laser source leaves the melt, it solidifies quickly. During fast solidification VC and  $VC_x$  develop through heterogeneous nucleation and grain expansion of VC nuclei. The matured  $VC_x$  strengthening components will be disseminated at grain boundaries and in austenite grains due to nucleation and progression.

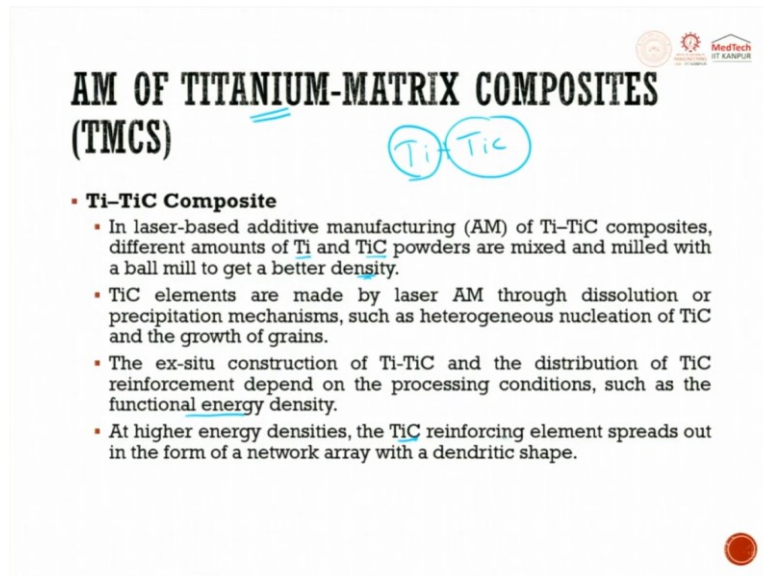
So, this is very important, the matured  $VC_x$  strengthening component will be disseminated at grain boundaries and in austenite grain due to nucleation and progression. When  $VC_x$  phase becomes bulky, grain expansion pushes them towards grain boundaries. The  $VC_x$  phase are retained within a austinite grain.

As laser AM have a quick solidification process, few V and C gets diffused into austenite solution, solid solution. So, in iron it was we saw very interestingly iron with  $TiB_2$   $TiC$

tungsten carbide and vanadium carbide. These are the four prominently used metal matrix composites made from additive manufacturing. Here now, we were only focusing towards the grain, grain boundary, grain refinement, Marangoni convection, flowing, dispersion and the other things, we never discussed about process, process parameters.

And now comes the shape factor, size factor of the additive manufacture parts. All these things make it really a complex phenomenon for making metal matrix composite through additive manufacturing but it is a growing area and is going to pick up lot of momentum.

(Refer Slide Time: 29:11)



**AM OF TITANIUM-MATRIX COMPOSITES (TMCS)**

*(Handwritten: Ti TiC)*

- **Ti-TiC Composite**
  - In laser-based additive manufacturing (AM) of Ti-TiC composites, different amounts of Ti and TiC powders are mixed and milled with a ball mill to get a better density.
  - TiC elements are made by laser AM through dissolution or precipitation mechanisms, such as heterogeneous nucleation of TiC and the growth of grains.
  - The ex-situ construction of Ti-TiC and the distribution of TiC reinforcement depend on the processing conditions, such as the functional energy density.
  - At higher energy densities, the TiC reinforcing element spreads out in the form of a network array with a dendritic shape.

Now let us move to titanium and titanium carbide reinforced composite. The laser based additive manufacturing of Ti TiC composite different amount of Ti and TiC powder are mixed and milled with the ball mill to get a better density. Now you see Ti and TiC are taken separately and they are ball milled. The TiC elements are made by laser AM through dissolution or precipitation mechanism such as heterogeneous nucleation of TiC and the growth of grain.

The ex-situ construction of Ti, TiC in situ is during the process, Ex-situ is outside the process of Ti and TiC and the dispersion of TiC reinforcement depending on the processing condition, such as functional energy density. At higher energy densities, the TiC reinforcing element spreads out in the form of a network array with the dendritic shapes.

(Refer Slide Time: 30:18)

## AM OF TITANIUM-MATRIX COMPOSITES (TMCS)

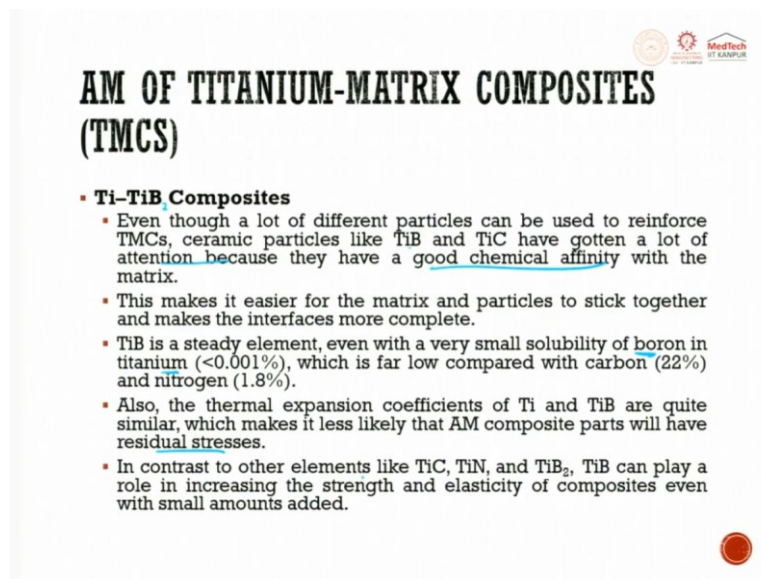
### ▪ Ti-TiC Composite

- At lower energy densities, the TiC gets smaller and spreads out more evenly.
- The lower energy density can also change the shape of TiC from rougher dendritic to whisker-like to lamellar.
- Higher scanning speeds cause faster cooling rates, which means there isn't enough time for TiC to grow in the composites.
- This leads to changes and improvements in the microstructure.

At lower energy densities, the TiC gets smaller and spreads out more evenly. The lower energy density can also change the shape of the TiC from rough dendritic to a whisker like to lamellar it can do. So, rough dendrite so now what is happening is the energy levels whatever is there during the process, it can also change the shape of TiC formation.

Higher scanning speeds causes faster cooling rate, which means that there is not enough time for TiC to grow in the composite. This leads to change in improvement in the microstructure. So lower energy densities, so TiC gets smaller when you have higher speed rates, you can see the TiCs are formed, which means that is not enough time for TiC to grow in the composite. So that also tries to change the property behaviour.

(Refer Slide Time: 31:28)



**AM OF TITANIUM-MATRIX COMPOSITES (TMCS)**

- **Ti-TiB Composites**
  - Even though a lot of different particles can be used to reinforce TMCs, ceramic particles like TiB and TiC have gotten a lot of attention because they have a good chemical affinity with the matrix.
  - This makes it easier for the matrix and particles to stick together and makes the interfaces more complete.
  - TiB is a steady element, even with a very small solubility of boron in titanium (<0.001%), which is far low compared with carbon (22%) and nitrogen (1.8%).
  - Also, the thermal expansion coefficients of Ti and TiB are quite similar, which makes it less likely that AM composite parts will have residual stresses.
  - In contrast to other elements like TiC, TiN, and TiB<sub>2</sub>, TiB can play a role in increasing the strength and elasticity of composites even with small amounts added.

When we talk about Ti TiB composite so, TiB<sub>2</sub> or TiB people say even though a lot of different particles can be used to reinforce TiC, titanium matrix composites. Ceramic particles like TiB and TiC have gotten a lot of attention because they have good chemical stability, like VC it tries to decompose tungsten carbide, it also tries to decompose there. This makes it easier for the matrix and the particles to stick together and make the interface more complete.

TiB is a steady element even with a very small solubility of boron in titanium, which is far low compared to that of carbon and nitrogen. Also, the thermal expansion coefficient of Ti and TiB are quite similar, which makes it less likely that additive manufacture composite parts will have residual stresses. In contrast to the other elements like TiC, TiN, TiB<sub>2</sub>, TiB can also play a role in increasing the strength and elasticity of the composite.

(Refer Slide Time: 32:47)

## AM OF TITANIUM-MATRIX COMPOSITES (TMCS)

- **Solidification Phases of Ti-TiB Composite**
  - Schematic presentation for the formation of TiB phase from the in-situ reaction within Ti and TiB<sub>2</sub> particles,
  - a) Powder mixture with good dispersion of TiB<sub>2</sub>, surrounded by bigger Ti powders prior to sintering,
  - b) In-situ reaction develops needle-like TiB, semi-reacted TiB<sub>2</sub>, and unreacted TiB<sub>2</sub>.

A. Sababhi Namini and M. Asadollah, "Microstructural characterization and mechanical properties of spark plasma-sintered TiB<sub>2</sub>-reinforced titanium matrix composite," Powder Metall., vol. 60, pp. 32–38, 2017, doi: 10.1080/00325999.2016.1268009

So the solidification phase of TiB composite, you can see here TiB<sub>2</sub> is formed and this is what is Ti. So, here in situ semi reactive TiB<sub>2</sub> so this forms in situ formation of TiW is there and here you see these are all unreacted TiB<sub>2</sub>. The schematic representation for the formation of TiB phase from the in situ reaction within Ti and TiB<sub>2</sub> particles is shown here. The powder mixture with good dispersion of TiB<sub>2</sub> surrounded by bigger Ti powder prior to sintering is like this, then during in situ reaction develops needle like TiB semi reacted TiB<sub>2</sub> and unreacted TiB<sub>2</sub> are formed.

(Refer Slide Time: 33:45)

## AM OF TITANIUM-MATRIX COMPOSITES (TMCS)

- **Solidification Phases of Ti-TiB Composite**
  - Before sintering, the powder mixture shows that the TiB<sub>2</sub> particles are well mixed with the larger Ti powders.
  - The in-situ reaction makes TiB, as well as TiB<sub>2</sub> that has partially reacted and TiB<sub>2</sub> that has not yet reacted.
  - Ti-TiB<sub>2</sub> powders are used to make in-situ Ti-TiB composites, and the process parameters are optimized to make this happen.
  - TiB<sub>2</sub> has a higher melting point than CP-Ti, so it needs a higher energy density to melt.
  - When Ti-TiB<sub>2</sub> composites are made, they have two phases: -Ti and TiB<sub>2</sub>.
  - The in-situ reaction occurs between TiB<sub>2</sub> and Ti through the diffusional removal of boron (B) from TiB<sub>2</sub> or by melting and successive solidification of TiB.

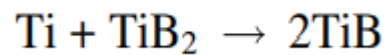
$$\text{Ti} + \text{TiB}_2 \rightarrow 2\text{TiB} \quad (12)$$

So, the solidification phase of TiB, Ti in TiB is same. Before sintering the powder mixture shows that the TiB<sub>2</sub> particles are well dispersed with the larger Ti powder. TiB<sub>2</sub> is dispersed

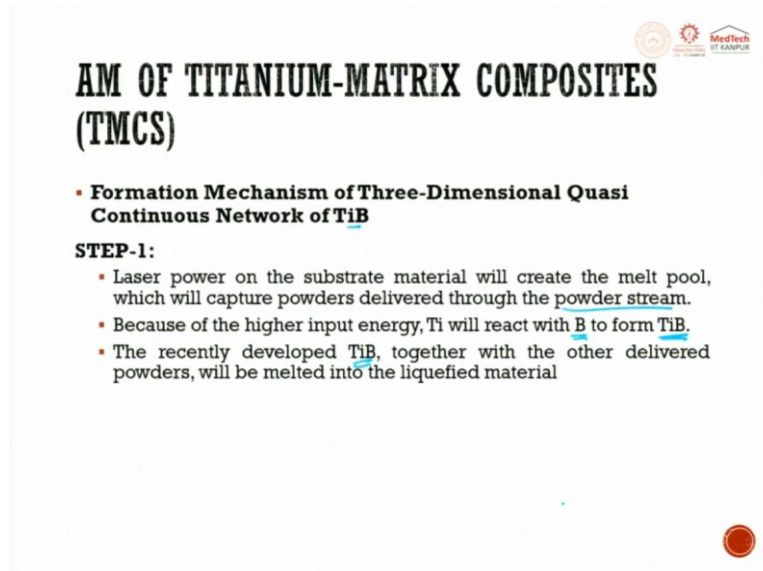


properly. With the in situ reaction makes TiB as well as TiB<sub>2</sub> that are partially reacted and the TiB<sub>2</sub> that are not yet reacted. Ti TiB<sub>2</sub> powders are used to make in situ TiB composite and the process parameters are optimized to make this happen.

TiB<sub>2</sub> has the highest melting point than CP closely packed titanium. So, it needs a higher energy density to melt. When Ti and TiB<sub>2</sub> composites are made, they have two phases Ti and TiB<sub>2</sub>. The in situ reaction occurs between TiB<sub>2</sub> and Ti through the diffusional removal of boron from TiB<sub>2</sub> or by melting or successful solidification of TiB.



(Refer Slide Time: 34:54)



**AM OF TITANIUM-MATRIX COMPOSITES (TMCS)**

- **Formation Mechanism of Three-Dimensional Quasi Continuous Network of TiB**

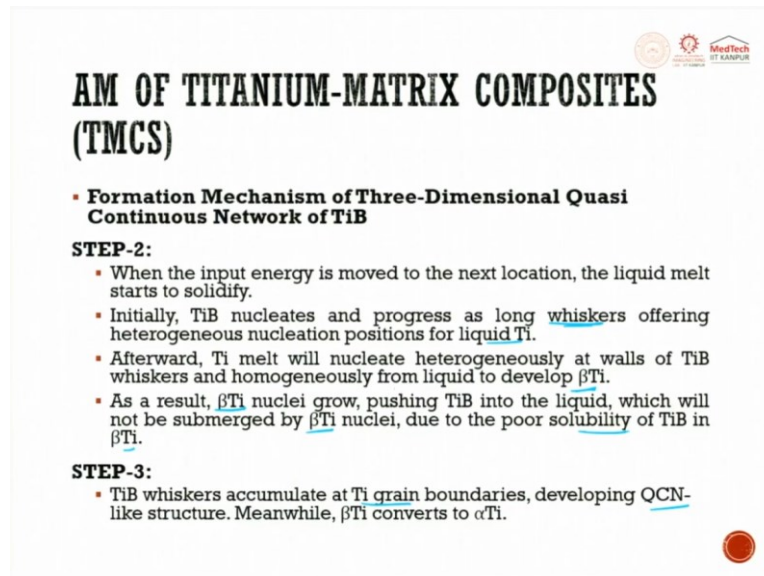
**STEP-1:**

- Laser power on the substrate material will create the melt pool, which will capture powders delivered through the powder stream.
- Because of the higher input energy, Ti will react with B to form TiB.
- The recently developed TiB, together with the other delivered powders, will be melted into the liquefied material

So, the formation mechanism of a three-dimensional quasi continuous network of the TiB is discussed here. The step one is laser power on the substrate material will create the melt pool, which will capture powder delivered through a powder stream. Because of the higher input energy Ti will react with B to form TiB. The recently developed TiB together with the other deliverable powder will be melt into liquefied material. This will be step one.



(Refer Slide Time: 35:32)



## AM OF TITANIUM-MATRIX COMPOSITES (TMCS)

- **Formation Mechanism of Three-Dimensional Quasi Continuous Network of TiB**

**STEP-2:**

- When the input energy is moved to the next location, the liquid melt starts to solidify.
- Initially, TiB nucleates and progress as long whiskers offering heterogeneous nucleation positions for liquid Ti.
- Afterward, Ti melt will nucleate heterogeneously at walls of TiB whiskers and homogeneously from liquid to develop  $\beta$ Ti.
- As a result,  $\beta$ Ti nuclei grow, pushing TiB into the liquid, which will not be submerged by  $\beta$ Ti nuclei, due to the poor solubility of TiB in  $\beta$ Ti.

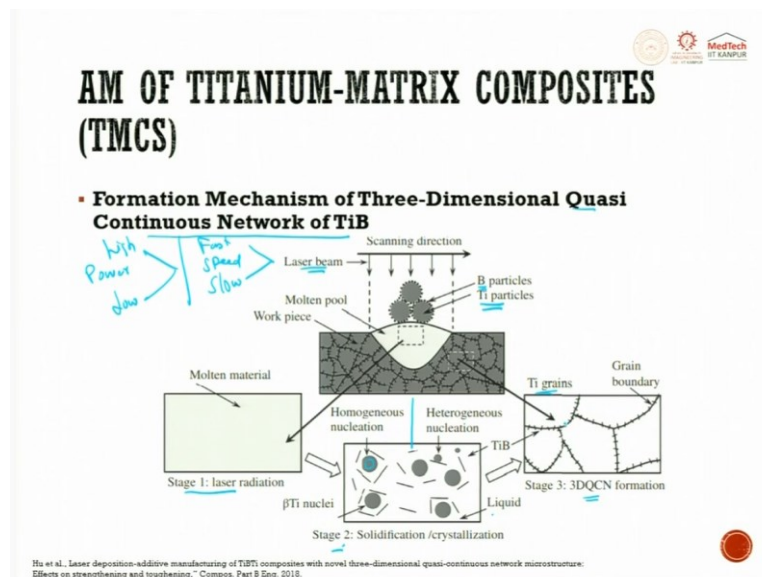
**STEP-3:**

- TiB whiskers accumulate at Ti grain boundaries, developing QCN-like structure. Meanwhile,  $\beta$ Ti converts to  $\alpha$ Ti.

The step two, will be when the input energy is moved to the next location. The liquid melt starts to solidify. Initially TiB nucleates and progress as long whiskers offering heterogeneous nucleation position for liquid Ti. Afterwards, Ti melt will nucleate heterogeneously at walls of TiB whisker and homogeneously from liquid to develop  $\beta$ Ti. So, the step sequence is very clearly written. Initially, TiB nucleates and progress into whisker, it forms a small lengthy whisker so that means to say diameter is very small, length is very high. Offering heterogeneous nucleation position for liquid Ti.

As a result,  $\beta$ Ti nuclei grow, pushes TiB into the liquid which will not be submerged by  $\beta$ Ti nuclei, due to the poor solubility of TiB in  $\beta$ Ti. So, we are just saying how is this  $\beta$ Ti coming and how is it getting formed in nucleation. So, that these composites can be formed. Step three will be TiB whisker accumulates at Ti with grain boundaries develop QCN like structure. Meanwhile,  $\beta$ Ti gets converted into  $\alpha$ Ti.

(Refer Slide Time: 37:15)



The formation mechanism of three-dimensional quasi continuous network  $\text{TiB}_2$ , I am trying to deal this in detail because the schematic diagram whatever we have present in here, will try to explain. Almost in the similar fashion you will have for ferrous also. SS 316L also we will have a say a similar mechanism which is going on.

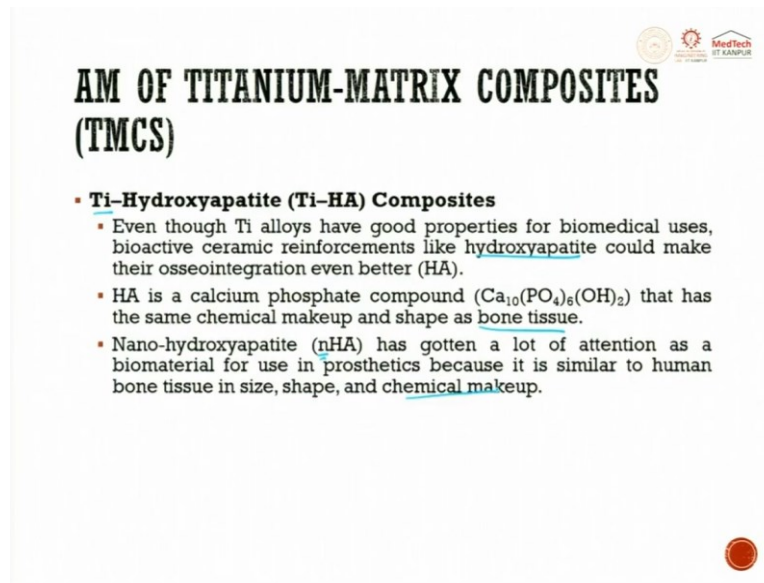
So, you have to go back to the phase diagram and then do it. So here if you see Ti particles along with B, where  $r_b$  is located around it. It is a schematic diagram so they are located around it. So now what we do is we keep it as a workpiece, now we try to expose it to laser beam. In laser beam, there are two things fast, slow scan and then you have another two more which is nothing but high power and low.

So, these two this is for power. This is for speed. So, with this what will happen, you will try to melt the material, so a pool is getting formed. So, when the pool is formed, you see first in this laser radiation you will see completely it is molten. Now in the second stage what happens is you have two things. One is called as homogeneous nucleation, the other one is called as heterogeneous nucleation.

Under homogeneous nucleation what you can see is you can see there, these particles are there and then these particles are  $\beta\text{Ti}$ , these are  $\beta\text{Ti}$  nuclei. So, it is there and then you have a whisker like structure, when you try to see the heterogeneous nucleation you will see that the spots of  $\beta\text{Ti}$  are there and then you also have some amount of small reinforcements which are getting formed.

When it goes to this phase is called as a solidification phase and under cooling also happens here. Now from the solidification phase, it will try to move towards the last phase of DQCN formation which is nothing but dimensional quasi continuous network formation. You can see here this is the grain boundary, you have Ti grains and then TiB sitting along the grain boundary. So this is how you try to get this TiB getting formed.

(Refer Slide Time: 39:41)



The slide is titled "AM OF TITANIUM-MATRIX COMPOSITES (TMCS)" in a bold, black, serif font. In the top right corner, there are three logos: a circular logo with a sun-like symbol, a red logo with a gear-like symbol, and a logo for "MedTech" with "VT KANPUR" below it. The main content is a bulleted list under the heading "▪ Ti-Hydroxyapatite (Ti-HA) Composites". The list contains three items, each starting with a red square bullet. The first item discusses the benefits of hydroxyapatite for osseointegration. The second item defines HA as a calcium phosphate compound with its chemical formula  $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$  and notes its similarity to bone tissue. The third item mentions nano-hydroxyapatite (nHA) and its use in prosthetics. The slide has a white background with a thin black border on the right side. A small red circular logo is visible in the bottom right corner of the slide area.

**AM OF TITANIUM-MATRIX COMPOSITES (TMCS)**

- **Ti-Hydroxyapatite (Ti-HA) Composites**
  - Even though Ti alloys have good properties for biomedical uses, bioactive ceramic reinforcements like hydroxyapatite could make their osseointegration even better (HA).
  - HA is a calcium phosphate compound ( $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ ) that has the same chemical makeup and shape as bone tissue.
  - Nano-hydroxyapatite (nHA) has gotten a lot of attention as a biomaterial for use in prosthetics because it is similar to human bone tissue in size, shape, and chemical makeup.

So, you can also try to do with hydroxyapatite which is very common nowadays used for biomedical applications. So, titanium mixed with hydroxyapatite composites for making bio implants. Here the bio implant has to have cell adhesion plus it has to have strength plus it has to have toughness. So, they try to mix all these things, even though Ti alloys have good properties for biomedical use, bioactive ceramic reinforcement like hydroxyapatite could make the osseointegration even better.

HA hydroxyapatite is a calcium phosphate compound that has the same chemical makeup and shape as bone tissue. So, we are trying to mix these two. Nano hydroxyapatite which is n has gotten a lot of attention as the biomaterials for use in prosthetics, because it is similar to human bone tissue in size, shape and chemical makeup.

(Refer Slide Time: 40:50)

**AM OF TITANIUM-MATRIX COMPOSITES (TMCS)**

- **Solidification Phases of Ti-HA Composite**
  - The reactions that take place through the LPBF process

$$\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2 \rightarrow \text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_{2-x} + x\text{H}_2\text{O}(\text{gas}) \quad (13)$$

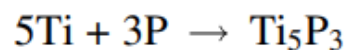
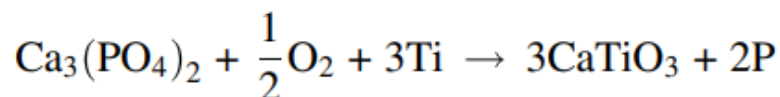
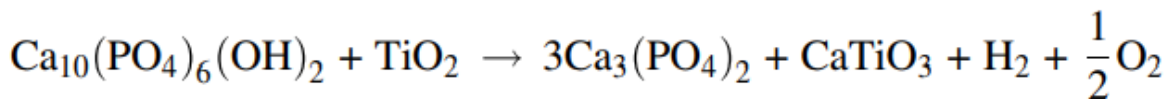
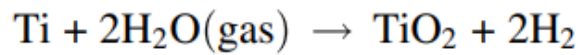
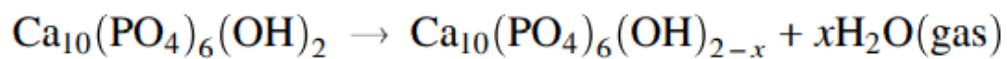
$$\text{Ti} + 2\text{H}_2\text{O}(\text{gas}) \rightarrow \text{TiO}_2 + 2\text{H}_2 \quad (14)$$

$$\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2 + \text{TiO}_2 \rightarrow 3\text{Ca}_3(\text{PO}_4)_2 + \text{CaTiO}_3 + \text{H}_2 + \frac{1}{2}\text{O}_2 \quad (15)$$

$$\text{Ca}_3(\text{PO}_4)_2 + \frac{1}{2}\text{O}_2 + 3\text{Ti} \rightarrow 3\text{CaTiO}_3 + 2\text{P} \quad (16)$$

$$5\text{Ti} + 3\text{P} \rightarrow \text{Ti}_5\text{P}_3 \quad (17)$$

So if you see here, the solidification phase of titanium with hydroxyapatite composites, the reaction takes place through the laser powder bed fusion method.



So this is a very, very interesting phase.

(Refer Slide Time: 41:38)

## AM OF TITANIUM-MATRIX COMPOSITES (TMCS)

### ▪ Solidification Phases of Ti-HA Composite

- The LPBF phase generation method for Ti-nHA is as follows: Ca/P components react with phase to create  $Ti_5P_3$ ,  $Ca_3(PO_4)_2$ ,  $CaTiO_3$ , and  $Ti_xO$  during HA breakdown.
- $Ti_5P_3$  and  $Ca_3(PO_4)_2$  remain dispersed throughout the matrix.  $Ca_3(PO_4)_2$  remains after  $CaTiO_3$  synthesis.
- Low oxygen absorption during production causes  $Ti_xO$  phase, not  $TiO_2$ .
- HA's oxygen diffuses into Ti matrix and creates titanium oxides.
- Faster LPBF solidification causes saturation, forming  $Ti_xO$ . Long lath-shaped grains are CP- structures.
- Ti's nHA in Ti matrix forms tiny acicular-shaped grains.

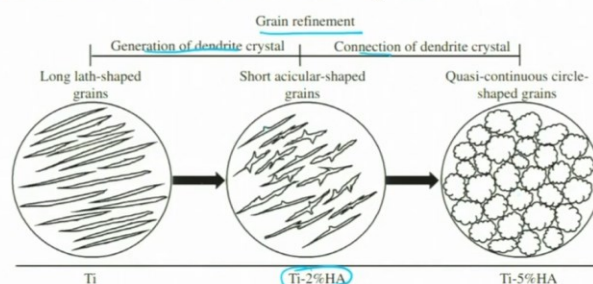
The laser powder bed fusion phase generation method for Ti-nano hydroxyapatite is as follows. Calcium phosphate component reacts with a phase to create  $Ti_5P_3$  then  $Ca_3P_4$  twice,  $CaTiO_3$  and  $Ti_x$  which we have set to  $Ti_xO$  during hydroxyapatite breaking. The  $Ti_5P_3$  and calcium  $PO_4$  twice remains dispersed throughout the matrix. So,  $CaPO_3$  remained after  $CaTiO_3$  is synthesized.

The low oxygen absorption during the production causes  $Ti_xO$  phase not  $TiO_2$ . The hydroxyapatite oxygen diffused into Ti matrix and creates titanium oxide. The faster laser powder bed fusion solidification causes saturation forming  $Ti_xO$ . Long lath-shaped grains and the CP structures, close packed structures. Ti nano hydroxyapatite in Ti matrix forms tiny acicular shaped grains. So this is what it is.

(Refer Slide Time: 43:04)

## AM OF TITANIUM-MATRIX COMPOSITES (TMCS)

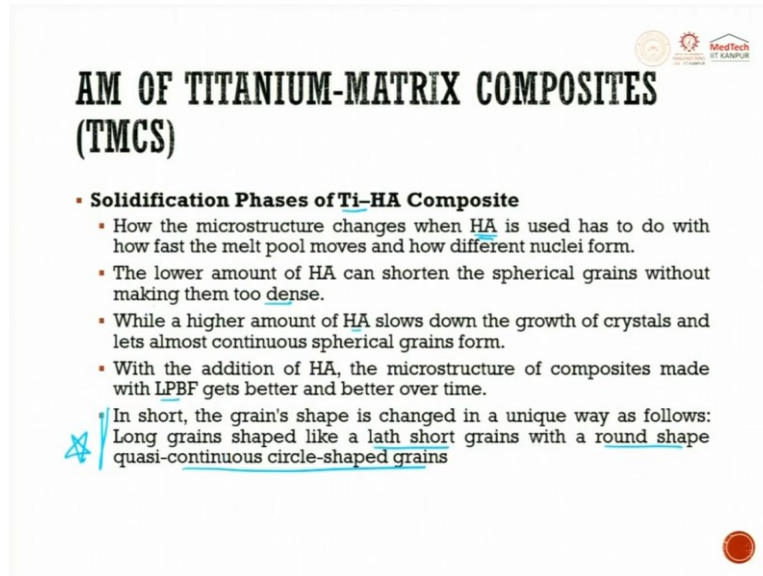
### ▪ Solidification Phases of Ti-HA Composite



Schematic presentation of the microstructural development in pure Ti, and Ti-2%HA and Ti-5%HA composites manufactured through LPBF techniques.

Solidification phase of Ti hydroxyapatite component, grain refinement there are two stages one is generation of dendrite crystal. The other one is connection of dendrite crystal. So, you have long lath shaped grains, and then this on heating will try to do with 2% of Hydroxyapatite will try to form short acicular shaped grains, so you see here, these are all acicular shaped grains and then this on further mixing with hydroxyapatite to 5% form quasi continuous circle shaped grains. So with the 0% only Ti or Ti+2% HA and with 5% HA you form generation of dendritic crystals and then here you will try to have connection of dendritic crystals.

(Refer Slide Time: 44:01)



The slide is titled "AM OF TITANIUM-MATRIX COMPOSITES (TMCS)" in a bold, black, serif font. In the top right corner, there are three logos: a circular logo with a gear, a red logo with a gear, and a logo for "MedTech". The main content is a bulleted list under the heading "Solidification Phases of Ti-HA Composite". The list includes four points about microstructure changes with HA, followed by a summary statement. A blue star icon is next to the summary. A red circular logo is in the bottom right corner.

## AM OF TITANIUM-MATRIX COMPOSITES (TMCS)

- **Solidification Phases of Ti-HA Composite**
  - How the microstructure changes when HA is used has to do with how fast the melt pool moves and how different nuclei form.
  - The lower amount of HA can shorten the spherical grains without making them too dense.
  - While a higher amount of HA slows down the growth of crystals and lets almost continuous spherical grains form.
  - With the addition of HA, the microstructure of composites made with LPBF gets better and better over time.

★ In short, the grain's shape is changed in a unique way as follows: Long grains shaped like a lath short grains with a round shape quasi-continuous circle-shaped grains

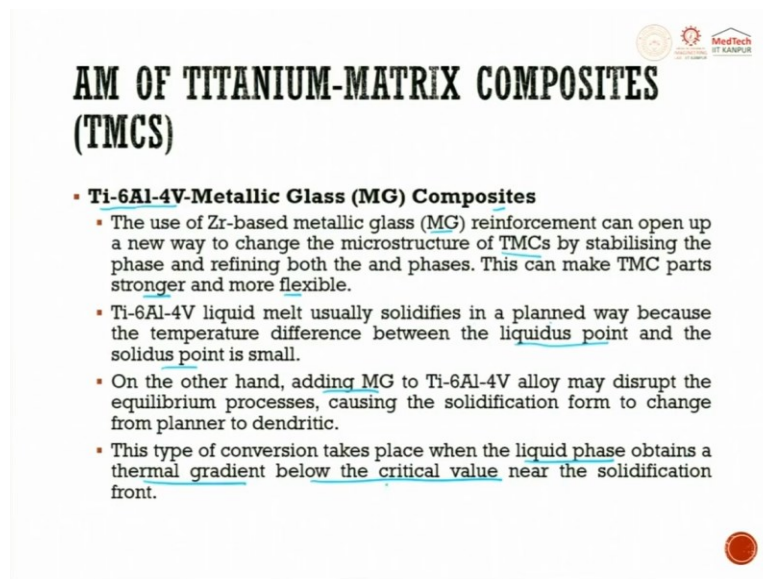
The solidification phase of Ti hydroxyapatite composite is how the microstructure changes when hydroxyapatite is used has to be with how fast the melting pool moves and how different nuclei forms. So all these things are very important to make a very good titanium which are titanium reinforced hydroxyapatite.

The lower amount of Hydroxyapatite can shorten the spherical grain without making them too dense. While a higher amount of Hydroxyapatite slow down the growth of crystal and let almost continuous spherical grain form, with the addition of hydroxyapatite the microstructure of composite made with LPBF gets better and better over time.

In short, the grains shape is changed in a unique way as follows, long grains shaped like a lath short grains with a round shape quasi continuous circle shape. This is very important you should know. The unique way follows long grain shape like lath short grains with a round shape quasi continuous circle shaped grains.



(Refer Slide Time: 45:20)



The slide is titled "AM OF TITANIUM-MATRIX COMPOSITES (TMCS)" in a bold, black, serif font. In the top right corner, there are three logos: a circular logo with a gear, a red logo with a gear, and a red logo with the text "MedTech". The main content is a bulleted list under the heading "Ti-6Al-4V-Metallic Glass (MG) Composites". The list contains four items, each starting with a red square bullet. The text is in a black, sans-serif font. The first item discusses the use of Zr-based metallic glass (MG) reinforcement. The second item discusses the solidification of Ti-6Al-4V liquid melt. The third item discusses the effect of adding MG to Ti-6Al-4V alloy. The fourth item discusses the conversion of the liquid phase. In the bottom right corner, there is a red circular logo.

## AM OF TITANIUM-MATRIX COMPOSITES (TMCS)


- **Ti-6Al-4V-Metallic Glass (MG) Composites**
  - The use of Zr-based metallic glass (MG) reinforcement can open up a new way to change the microstructure of TMCs by stabilising the phase and refining both the and phases. This can make TMC parts stronger and more flexible.
  - Ti-6Al-4V liquid melt usually solidifies in a planned way because the temperature difference between the liquidus point and the solidus point is small.
  - On the other hand, adding MG to Ti-6Al-4V alloy may disrupt the equilibrium processes, causing the solidification form to change from planner to dendritic.
  - This type of conversion takes place when the liquid phase obtains a thermal gradient below the critical value near the solidification front.

Today, we also make Ti6 Al 4V metallic glass composites. So, metallic glass means they show properties of metal as well as glass. So, they undergo this glass transition temperature behaviour. The use of Zr based metallic glass MG reinforcement can open up a new way to change the microstructure of titanium metal matrix composite by stabilising the phase and reinforcing both the phase. This can make titanium metal matrix composite part stronger and more flexible.

The Ti6 Al 4V liquid melt usually solidifies in a planned way because the temperature difference between the liquidus point and the solidus point is very small. On the other hand, adding MG metallic glass to Ti6 Al 4V alloy may disrupt the equilibrium process causing the solidification form a change from planar to dendritic structure.


This type of conversion takes place when the liquid phase obtain a thermal gradient below the critical value near the solidification front. This is very important, takes place when the liquid phase obtains a thermal gradient, liquid phase obtains a thermal gradient below a critical value.

(Refer Slide Time: 46:59)



## AM OF TITANIUM-MATRIX COMPOSITES (TMCS)

- **Ti-6Al-4V-Metallic Glass (MG) Composites**
  - The critical thermal gradient  $\delta T/\delta X_{crit}$  is given by
$$\frac{\delta T}{\delta X_{crit}} = - \frac{C_0}{D_L/R} \frac{1-k}{k} \frac{\delta T_L}{\delta C} \quad (18)$$
where  $C_0$  is the solute concentration,  $D_L$  is the solute diffusion coefficient,  $R$  is the solidification rate, and  $k$  is the solute partition coefficient, associated with the solidification limit among the liquidus and solidus temperatures
  - Because of the different density of Ti-6Al-4V and MG melts, a gravity force will act on MG melt to settle down the melt. The dynamic viscosity,  $\mu$ , for a liquid (kg/(m.s)) is given by
$$\mu = \frac{16}{15} \sqrt{\frac{m}{\sigma_B T}} \gamma \quad (19)$$
where  $m$  is the atomic mass (amu),  $\gamma$  is the surface tension (N/m),  $T$  is the temperature (K), and  $\sigma_B$  is the Boltzmann constant (J/K).



So the critical thermal gradient  $\delta T/\delta X$  is given by:

$$\frac{\delta T}{\delta X_{crit}} = - \frac{C_0}{D_L/R} \frac{1-k}{k} \frac{\delta T_L}{\delta C}$$

where  $C_0$  is the solute concentration,  $D_L$  is the solute diffusion coefficient,  $R$  is the solidification rate, and  $k$  is the solute partition coefficient, associated with the solidification limit among the liquidus and solidus temperatures.

Because of the different density of Ti-6Al-4V and MG melts, a gravity force will act on MG melt to settle down the melt. The dynamic viscosity,  $\mu$ , for a liquid (kg/(m.s)) is given by:

$$\mu = \frac{16}{15} \sqrt{\frac{m}{\sigma_B T}} \gamma$$

where  $m$  is the atomic mass (amu),  $\gamma$  is the surface tension (N/m),  $T$  is the temperature (K), and  $\sigma_B$  is the Boltzmann constant (J/K).

(Refer Slide Time: 47:58)

## AM OF TITANIUM-MATRIX COMPOSITES (TMCS)

### ▪ Ti-6Al-4V-Metallic Glass (MG) Composites

- Theoretically, owing to a higher density and viscosity, the MG melt leans to separate from the Ti-6Al-4V melt. In addition, the  $\beta$  phase becomes stable by Cu and Ni and then passes through solidification, having the higher melting temperature
- The dendrite formation discards solute elements (Cu, Ni, and Al) through the solid/liquid interface to supercooled melt, which enriches the melt pool with MG contents leading to the initiation of amorphous phases
- In addition, the faster cooling process restricts the growth of the amorphous phases, resulting in the MG as nanobands
- However, the MG nanobands can pass a partial crystallization during continual heating of layer-to-layer deposition. Thereby, a hard/soft nanostructured Ti-6Al-4V/MG composite is formed with partially crystallized MG reinforcing elements (hard phase), embedded in  $\beta$  grains (soft phase).

Theoretically, owing to the higher density and viscosity the MG melt leans to separate from the Ti6 Al 4V melt. In addition, the  $\beta$  phase becomes stable by copper and nickel. And then, passes through a solidification having a higher melting temperature. The dendritic formation, these are the elements which play a very important role to do the super cooling of melt and which enriches melt pool with MG.

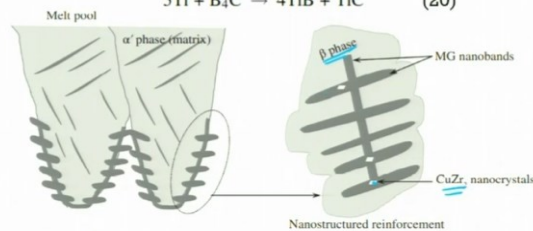
Addition of faster cooling process restricts the growth of amorphous phase MG. And however, MG nano bands can pass a partial crystallisation during continual heating of layer by layer deposition. Thereby a hard soft nanostructure melt composite can be formed by using AM structure.

(Refer Slide Time: 48:55)

## AM OF TITANIUM-MATRIX COMPOSITES (TMCS)

### ▪ Ti-6Al-4V + B<sub>4</sub>C Pre-alloyed Composites

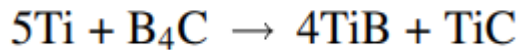
- TMCs manufactured from the mixture of Ti-6Al-4V + B<sub>4</sub>C powders with different volume contents of B<sub>4</sub>C follow the in-situ chemical reaction of



Schematic microstructure of the as-printed Ti-6Al-4V/MG composite

Shen et al. On the microstructure, mechanical properties and wear resistance of an additively manufactured Ti64/metallic glass composite. 2019.

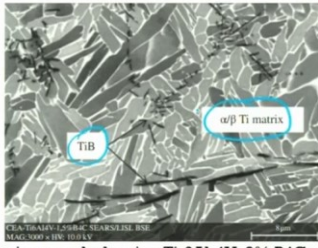
This is what is the mixture of boron carbide with Ti 6 Al 4V. So, you have a melt pool, you have an  $\alpha$  phase which is there and you see these are  $\beta$  phase and these are all MG nano bands which are formed in the reinforcement. And this copper, these are also copper Zr are also formed as nanocrystals during the process. So, TMC manufactured from the mixture of Ti6 Al 4V + B<sub>4</sub>C powder with different volume content of B<sub>4</sub>C follow the in situ chemical reaction of this.



(Refer Slide Time: 49:36)

### AM OF TITANIUM-MATRIX COMPOSITES (TMCS)

- **Ti-6Al-4V + B<sub>4</sub>C Pre-alloyed Composites**
  - The composite consists of a dual structure of  $\alpha/\beta$  Widmanstätten Ti matrix, enclosing with nonuniformly distributed TiB whiskers



SEM micrograph showing Ti-6Al-4V- 3% B<sub>4</sub>C composite

Pouret et al. Additive layer manufacturing of titanium matrix composites using the direct metal deposition laser process. Mater. Sci. Eng. A. 2016.

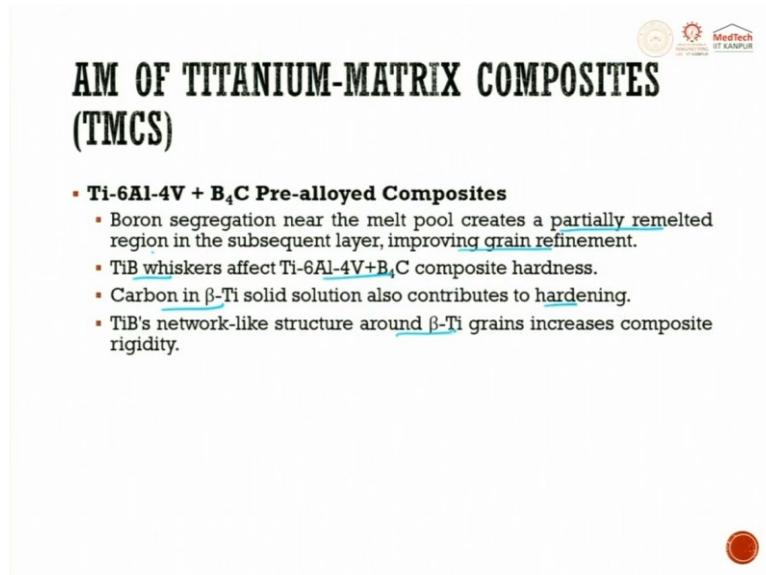
### AM OF TITANIUM-MATRIX COMPOSITES (TMCS)

- **Ti-6Al-4V + B<sub>4</sub>C Pre-alloyed Composites**
  - Ti<sub>4</sub>B affects solidification in several ways.  $\beta$ -Ti can form as the first solid phase during solidification based on the TiB phase diagram.
  - Boron rejects liquids when  $\beta$ -Ti grows, causing micro-segregation of B near grain boundaries and eutectic solidification.
  - Fine TiB whiskers stop grain expansion when the eutectic temperature rises.
  - $\beta$ -Ti grain variation may cause boron macro-segregation during solidification.
  - This refinement happens only under each additive layer, which should be non-melted.

So, this is for B<sub>4</sub>C pre-alloyed composite, you can see TiB and  $\alpha\beta$ Ti matrix. So, the Ti<sub>4</sub>B affects solidification in several ways.  $\beta$ Ti can form as a first solid phase during solidification based on Ti phase diagram. The boron rejects the liquid with  $\alpha\beta$  so, it is not necessary

everything will be accepted, it also can reject causing micro segregation of B near grain boundaries and eutectic solidification. Fine TiB whiskers stops grain expansion and  $\alpha$ Ti grain variations may cause boron macro segregation during solidification.

(Refer Slide Time: 50:21)

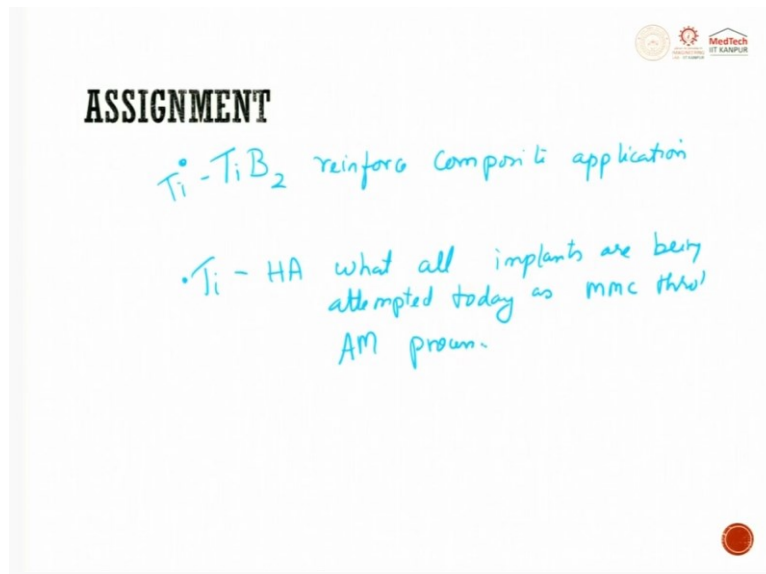


**AM OF TITANIUM-MATRIX COMPOSITES (TMCS)**

- **Ti-6Al-4V + B<sub>4</sub>C Pre-alloyed Composites**
  - Boron segregation near the melt pool creates a partially remelted region in the subsequent layer, improving grain refinement.
  - TiB whiskers affect Ti-6Al-4V+B<sub>4</sub>C composite hardness.
  - Carbon in  $\beta$ -Ti solid solution also contributes to hardening.
  - TiB's network-like structure around  $\beta$ -Ti grains increases composite rigidity.

So, the boron segregation near the melt pool creates a partial remelt region in the subsequent layer improving the grain structure. TiB whisker affects the Ti 6 Al 4V + B<sub>4</sub>C the carbon in the  $\beta$ Ti solution contributes to hardening and TiB network like structure around  $\beta$ Ti grain increases composite rigidity.

(Refer Slide Time: 50:49)



**ASSIGNMENT**

- Ti-TiB<sub>2</sub> reinforced composite application
- Ti-HA what all implants are being attempted today as mmc thro' AM process.

Now let us look at assignments. There are two assignments which I will give, so you try to see TiB<sub>2</sub> reinforced composite application, where do they use this metal matrix composite?

Next one is when we talk about Ti HA hydroxyapatite what all implants are being attempted today, as MMC through AM process? These two will give you an insight of the process or insight about the formation of the microstructure and other things. Thank you very much.