Surface Engineering for Corrosion and Wear Resistance Application
Prof. Indranil Manna
Department of Metallurgical and Materials Engineering
Indian Institute of Technology, Kharagpur

Lecture - 56
Laser Surface Engineering with Laser surface hardening and laser surface melting

(Refer Slide Time: 00:02)

Laser Assisted Surface Engineering (LSE)

Part II:

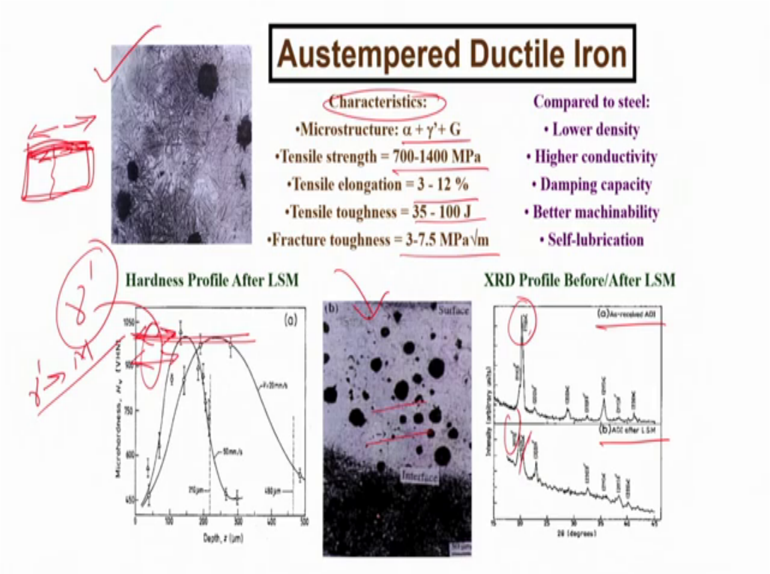
Only microstructural changes

(published results)

Welcome to the 56th lecture of Surface Engineering. In the previous lecture you just heard that we discussed about the possibilities of modifying the surface microstructure only without changing the composition. We discussed the fundamental aspects of it as to why such effects come in and what is it in case of steel vis a vis nonferrous metals and also how it affects in case of semiconductors or non metallic systems. We even discuss a surface texturing, which is basically creating certain pattern regular pattern onto the surface to improve tribological properties and so on.

Now, in this lecture we are going to pick up very specific examples from results which are already published in the literature and actually I will borrow heavily from our from results published from our own group at IIT Kharagpur. So, in this case as I said already that, we are only talking about changes of the shape size, identity, volume fraction, orientation and other things of the aggregates phase aggregates that we have onto the surface.

(Refer Slide Time: 01:29)



Austempered Ductile Iron

Characteristics:
- Microstructure: $\alpha + \gamma' + G$
- Tensile strength = 700-1400 MPa
- Tensile elongation = 3 - 12 %
- Tensile toughness = 35 - 100 J
- Fracture toughness = 3-7.5 MPa√m

Compared to steel:
- Lower density
- Higher conductivity
- Damping capacity
- Better machinability
- Self-lubrication

Hardness Profile After LSM

XRD Profile Before/After LSM

So, so let me move to the first example and after let me also tell you that microstructural changes that we are talking about we have we are mostly dealing with metallic systems and so we are dealing with metallic systems and we divide them mostly into two major bar scale steel and nonferrous alloys. So, I will pick up two examples say first one is; from austempered ductile iron which is basically a bainitic cast iron.

So, if you recall that in my cast iron what we mean is that we have at some point of during the cooling process or melting to solidification process we must intersect the eutectic isotherm. So, we end up getting ledeburite combination of cementite and austenite and subsequently the austenite transforms to pearlite. So, we have we end up end up getting transformed ledeburite at the room temperature.

Now, austempered ductile iron because of certain specific compositional effect, allows us to actually obtain first of all graphite in the form of spheroids. And, then because of certain heat treatment we actually end up getting a bainitic microstructure instead of pearlitic microstructure at room temperature largely bainitic. So, the typical microstructure will have a ferrite, retained austenite and graphite. We are talking about fairly high tensile strength of the material and reasonably higher now normally cast iron will have just 1 or 2 percent maybe less than 3 percent ductility, but here we are talking about tensile ductility as high as 10 percent or so. And that is possible because of this bainitic microstructure.

Also in addition to that we have both high tensile toughness and also higher fracture toughness. So, all these characteristics of austempered ductile iron or spheroidal graphitic iron with bainitic microstructure makes it a very very important material for various including engine blocks to various cast products. Like in this particular case we are talking about the application scope of ADI for excavator shovels. Now, let us not worry about exactly which component we are talking about what is important is normally cast iron when you heat and cool when you melt either surface or the bulk and then solidify you end up getting a typically a transform ledeburite microstructure.

So, the austempered structure is destroyed. So, the toughness and other tensile ductility and all those advantages are forfeited. Now, if that is that happens typically when you do for the bulk. Even in the surface, when you convert bainite into molten layer thin molten layer onto the surface and then allow self quenching you end up getting ledeburitic microstructure which will have a lot of not graphite anymore, but carbon will appear in the form of cementite. And these are hard interstitial compounds and as a result of which you get very high wear resistance, but you actually pay a price. And that price is because of solidification and the shrinkage associated with solidification process you end up developing residual tensile stress onto the surface.

So, if you have a component and in the surface if you develop residual tensile stress, then for whatever reasons if you form a crack that crack can easily propagate and this will lead to failure we do not want that should happen. So, if you take a component made out of ADI let us say this is a component made out of ADI and if you do surface melting then the surface will develop residual tensile stress. And the hardness profile typically will be sort of Gaussian like this so this is an experimental result. So, what is interesting is that you do have fairly high hardness, very high hardness higher than martensitic hardness. Because of the presence of cementite which is over 900 because hardness.

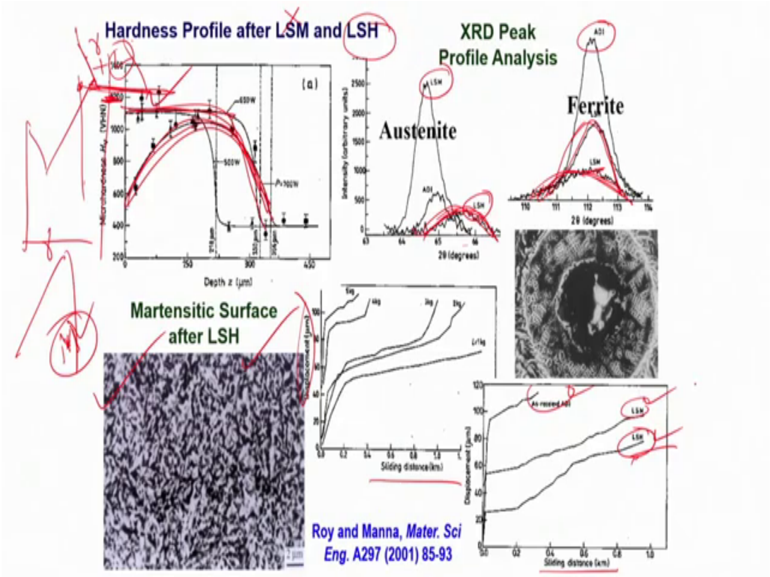
But that high hardness region is not at the surface, but below the surface. So, from the surface a certain region is actually fairly soft. And this softness comes from retained austenite. Because you have dissolved all the carbon in the liquid and when you quench the liquid transforms to tries to transform to martensite it cannot during the cooling process because of presence of very high amount of carbon in the melt. And, in the process you end up getting a microstructure or dendritic forms of the microstructure which is predominantly retained austenite. We all are aware that there are several problems with written austenite. First of all this written the austenite in the process of mechanical deformation may undergo martensitic transformation. And that would mean expansion and creation of enormous stress within the solid matrix leading to formation of micro cracks.

So, these are hidden micro cracks which may given in future and lead to catastrophic failure. So, this is dangerous we would rather like to avoid. The more important difficulties that the surface actually is fairly soft, because of the presence of high amount of retained austenite. So, this again is something we would rather avoid. So, we would like to so this is the starting microstructure of bainitic austempered ductile iron, bainitic cast iron.

And when you do surface melting you end up getting a microstructure which will have which will have these regions of carbon rich regions of semi molten or molten regions. But the most important fact is that this is essentially a ledeburitic microstructure. And hence because of presence of large amount of retained austenite the surface hardness is low and will have a Gaussian distribution. And, if you look at if you compare this the corresponding the microstructure if you probe by X-ray diffraction.

In case of as received ADI the peak for the ferrite or actually because of bainitic microstructure is fairly large which essentially means that the volume fraction of ferrite is much higher and volume fraction of retained austenite is much lower. On the other hand, when you do laser surface melting the volume fraction of gamma prime is much higher compared to the volume fraction of ferrite. So, the retained austenite region in this retained austenite volume fraction in this region or in the top microstructure here is much larger and that is what I was trying to explain is not desirable.

(Refer Slide Time: 08:33)



Hardness Profile after LSM and LSH

XRD Peak Profile Analysis

Martensitic Surface after LSH

Roy and Manna, *Mater. Sci Eng.* A297 (2001) 85-93

So, what we showed was that by very careful manipulation of process parameters instead of a Gaussian distribution of hardness profile you actually can get a very fairly flat hardness profile on to the surface. So, this is what we want how do we achieve this? We achieve this by ensuring that we have laser surface hardening and not laser surface melting. In other words, if you are looking at the let us say if this is the eutectic isotherm.

So, and if this is your composition, if you manage to heat up to this temperature and not going to the semi-solid region; so, this is the region which will have gamma plus liquid. So, form liquid may form if you cross this isotherm. If you do not cross this isotherm if you simply heat up to this region or if the composition is of lower carbon if you have somewhat like this if you heat up to this region and do not cross this liquidus line then solidus line then; obviously, you will retain entire solid.

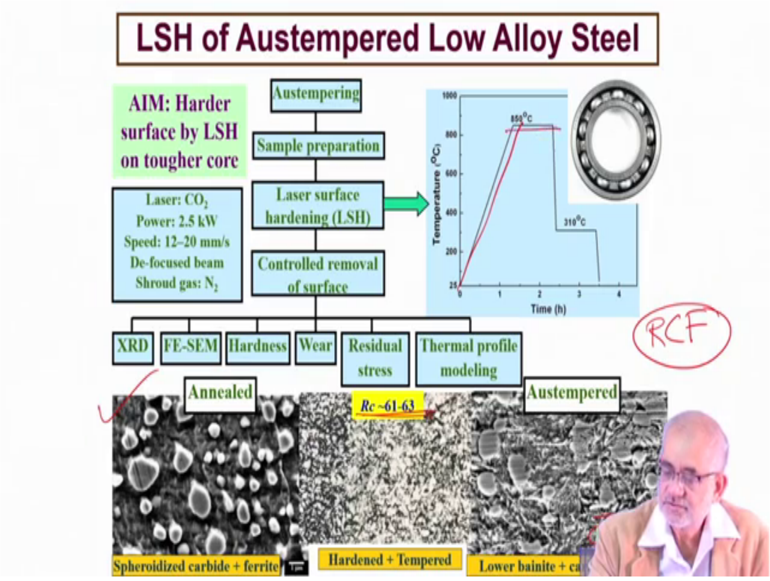
So, the entire heating effect will be confined to only solid. So, in the process when you quench; so when you heat and then when you quench by self quenching. So, you convert this to austenite and by quenching self quenching you convert this austenite into martensite and that is what you want. So, this is exactly the kind of microstructure that you develop. So, compared to this microstructure; here if you develop this kind of a microstructure this is predominantly martensitic and this is borne by the fact that when you do surface melting you have a very large austenite peak. So, the volume fraction of austenite is retained austenite is much larger.

But when you the do hardening then the volume fraction of austenite follows this profile. So, the total area under this curve is much lower and hence the volume fraction of austenite has to be much lower than the previous case. On the other hand, if you look at the ferrite peak then in or in normal condition of austempered ductile iron you have large ferrite volume fraction area under the peak is larger in case of surface melting this is much smaller. So, when you have surface melted ferrite is low, austenite is high. After hardening the volume fraction of ferrite is much higher and volume fraction of austenite is much lower.

So, when you get martensite predominantly martensitic microstructure the retained austenite volume fraction is marginal. And as a result of which you actually can get very high variance since of this is displacement as a function of sliding distance for abrasive wear condition. And, also what we realize is that the wear depth as a function of sliding distance is least when you have laser surface hardening compared to surface melting or in as received ADI.

So, if I start with austempered ductile iron stock of the solid and if I do surface hardening and we do not want and we do not allow melt to be formed. Then we end up creating not only higher hardness because of martensitic transformation, but also residual compressive stress and as a result of which the wear damages or wear loss will be least when we have hardening hardened surface, then compared to either as received austempered ductile iron or after surface melting.

(Refer Slide Time: 12:28)



LSH of Austempered Low Alloy Steel

AIM: Harder surface by LSH on tougher core

Laser: CO_2
Power: 2.5 kW
Speed: 12–20 mm/s
De-focused beam
Shroud gas: N_2

Austempering
Sample preparation
Laser surface hardening (LSH)
Controlled removal of surface

XRD
FE-SEM
Hardness
Wear
Residual stress
Thermal profile modeling

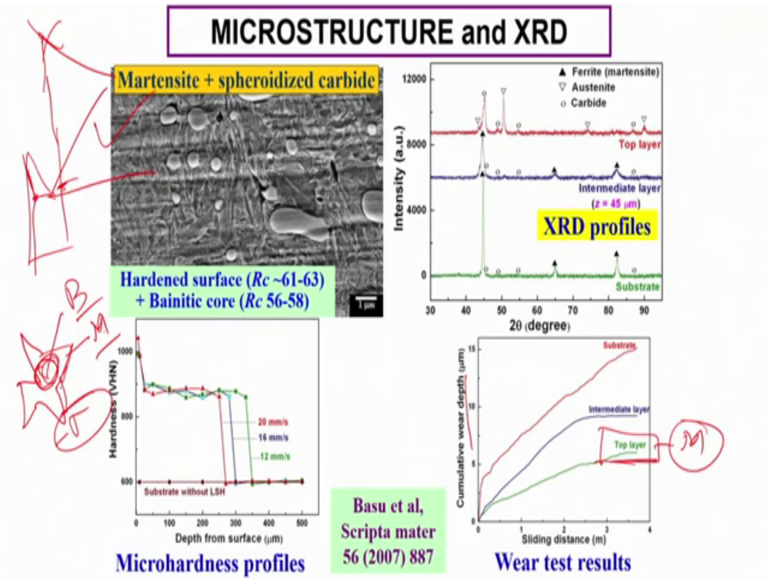
So, one has to know how to control the process parameters and this process parameters essentially in terms of power density and interaction time. So, we should heat for smaller period of time, allow reasonably high power density and with this combination we should be able to go and heat only up to this region and not cross this liquidus line a solidus line right. So, if we heat only up to this region and not go beyond then we are in all solid condition and then subsequent self quenching will produce such martensitic microstructure so that is the strategy.

The same strategy we applied for another kind of steel which is austempered low alloy high carbon steel the typical bearing steel material AISI 52100 and what we did there basically is. So, in a normal annealed condition this is the kind of a microstructure. So, these are the spheroids of carbides and in hardened and tempered condition typical hardness level is higher. So, in hardened and tempered condition you have tempered martensite, but in austempered condition which is bainitic microstructure.

You sacrifice some amount of hardness, but what is more important is that you also attain in the bargain a much higher toughness. And because of slight softening effect toughness increases and a property which is very important for all rotating parts called rolling contact fatigue. This property is significantly improved if we can create a microstructure with the which is bainitic instead of hardened and tempered.

So, this is the kind of typical hardening cycle one follows 850 would be the austenitizing temperature you quench actually you quench and then reheat and then you do tempering at about 300 degree centigrade. So, you get hardened and tempered structure.

(Refer Slide Time: 14:39)



MICROSTRUCTURE and XRD

Martensite + spheroidized carbide

Hardened surface (*Rc* ~61-63) + Bainitic core (*Rc* 56-58)

XRD profiles

Microhardness profiles

Basu et al, Scripta mater 56 (2007) 887

Wear test results

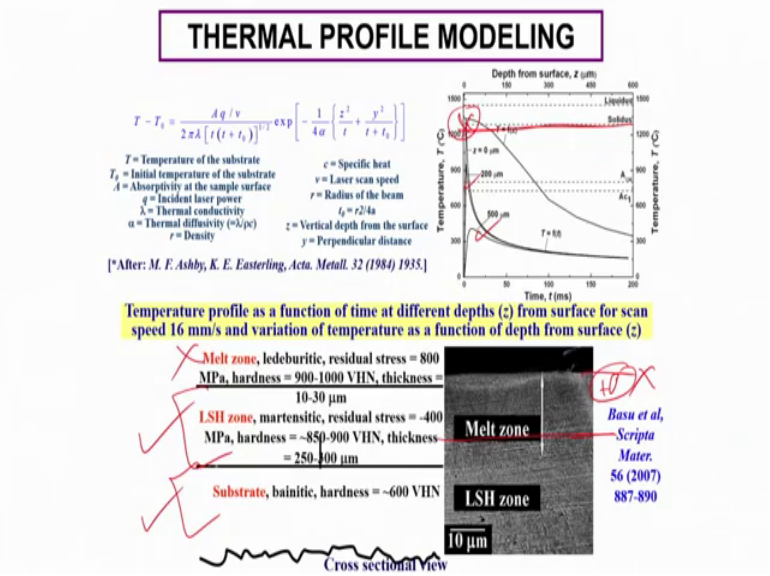
So, what we wanted to do now is to take this material and then try to bring in a microstructure which will be martensite along with spheroidized carbide. So, what we want is that we want the surface to be heated by laser controlled heating, confined heating which will again take it to up to the. So, now, we are talking about the steel portion. So, we are talking about 1 percent carbon so somewhere here.

So, we would like to heat maybe up to somewhere around this temperature, but not cross the so high that we cross the solidus temperature. So, we should not go all the way up here. So, we should confine the heating effect to such a level that we only go to austenite, pure austenite or austenite plus cementite in this double phase region. So, in the process what we can do is so we will have a gear component. So, we will have a gear component where the core will be bainite and the surface will be martensite. So, this is the combination that we want.

The advantage of having martensite onto the surface is not only higher hardness, but also residual compressive stress. And this residual compressive stress is possible when we convert austenite to martensite. So, again these are the diffraction patterns or the signatures of what we have phase aggregate wise onto the surface. So, this is a similar result that we want the top layer to undergo the least amount of wear. So, this is the wear depth and this is possible because of this marten predominantly martensitic microstructure.

So, you have bainitic core and hardens martensite onto the surface. This combination certainly is more desirable than hardened and tempered up to a greater depth. Because in that case we have softer code to absorb energy and as a result the rolling contact fatigue or the toughness or overall toughness of the material will be higher.

(Refer Slide Time: 17:03)



THERMAL PROFILE MODELING

$$T - T_0 = \frac{Aq/v}{2\pi\lambda\left[t(t+t_0)\right]^{1/2}}\exp\left[-\frac{1}{4\alpha}\left\{\frac{z^2}{t}+\frac{y^2}{t+t_0}\right\}\right]$$

T = Temperature of the substrate
T_0 = Initial temperature of the substrate
A = Absorptivity at the sample surface
q = Incident laser power
λ = Thermal conductivity
α = Thermal diffusivity (=$\lambda/\rho c$)
r = Density

c = Specific heat
v = Laser scan speed
r = Radius of the beam
$t_0 = r2/4a$
z = Vertical depth from the surface
y = Perpendicular distance

[*After: *M. F. Ashby, K. E. Easterling, Acta. Metall. 32 (1984) 1935.*]

Temperature profile as a function of time at different depths (z) from surface for scan speed 16 mm/s and variation of temperature as a function of depth from surface (z)

Melt zone, ledeburitic, residual stress = 800 MPa, hardness = 900-1000 VHN, thickness = 10-30 µm

LSH zone, martensitic, residual stress = -400 MPa, hardness = ~850-900 VHN, thickness = 250-300 µm

Substrate, bainitic, hardness = ~600 VHN

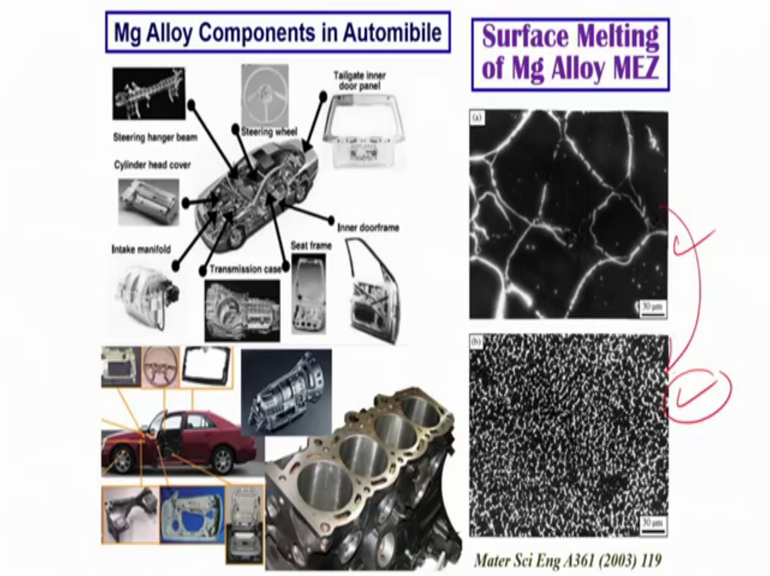
Cross sectional View

Basu et al, Scripta Mater. 56 (2007) 887-890

So, in order to do that actually it is important that we make sure that the surface melting is avoided. So, if you form surface melting then you end up getting certain higher amount of carbides, but more importantly this region because of the shrinkage follow suffered during solidification may develop a residual compressive residual tensile stress which is what we do not want.

So, either you grind off this portion or make sure that your heating process is going to cross not going to cross the solidus line. So, we do not want this to go too. So, you control the incident power density and interaction time such a way that the heating cycle would be say this one or this one, but not this one we do not want this one. So, that we do not cross the solidus line at all so there is no localized melting at all. And so this overall behavior this cross sectional view actually tells us that we do not want this part, we want this part and this is the underlying substrate.

(Refer Slide Time: 18:16)



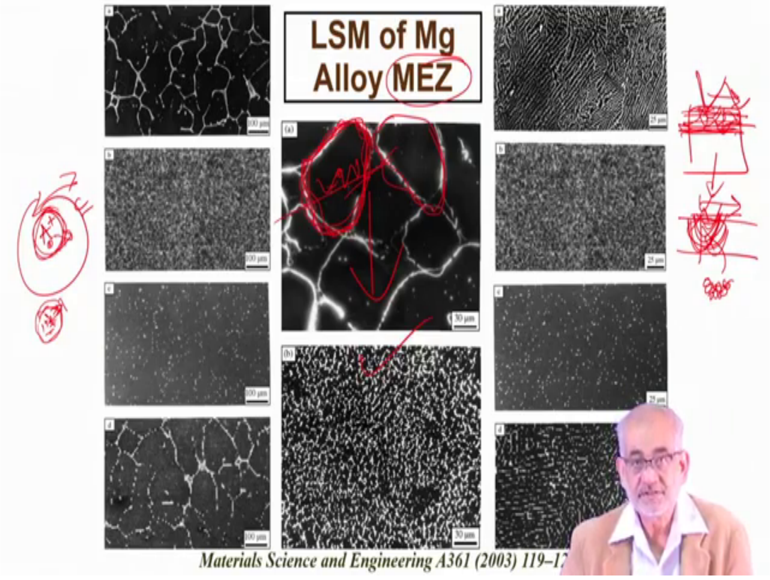
Mg Alloy Components in Automibile

Surface Melting of Mg Alloy MEZ

Mater Sci Eng A361 (2003) 119

Now, one can also take up examples from non ferrous alloys for example, here is an example. So, this is just to impress you with the various possibilities of components injuring components made from magnesium alloys possible magnesium alloy based components. And, we are going to discuss how do we create this microstructure from or how do we convert such course microstructure into such very ultra fine microstructure and gain certain advantages.

(Refer Slide Time: 18:48)



LSM of Mg Alloy MEZ

Materials Science and Engineering A361 (2003) 119–1

So, in order to understand that these are basically these microstructures are derived from components subjected to various kind of laser routines, laser surface engineering routines. But if you do so in the previous two cases I emphasize that we should remain below the solidus temperature; that means, we do not want to create formation of liquid either in small volume or large volume. Because liquefactions followed by solidification will create residual compressive stress.

But residual tensile stress which is what we do not want. But if we are dealing with magnesium or say aluminum alloys or such non ferrous alloys, low melting non ferrous alloys we can easily melt the surface. So, if this is a bulk component and if we are melting this surface so, if we have let us save such coarse microstructure then we can convert this by surface melting. So, we use a laser beam, we rested over the surface and allows melting up to a certain depth and then rapid solidification. Because this is a solid liquid interface maximum depth the solid liquid interface moves down to and then after the beam is withdrawn pulsed the pulse is off or the beam moves away from here to here.

So, by that time this region which actually so this is how the molten zone actually penetrated into the depth and this is a final solid liquid interface position. So, by the time the moves away so this portion will now go back. So, now the solid liquid interface will recede to the surface and when recedes; so, this region becomes solidified and this solidified microstructure will be extremely fine. So, the grain size will be extremely fine and this is exactly the effect we are seeing here.

So, from this microstructure purely by surface melting up to a certain depth from the surface we can convert the surface microstructure from being so coarse to so fine. And the advantage in this particular case we are dealing with a rare earth added magnesium alloy. So, these presence of these rare earths actually forms allows formation of certain inter metallic aluminates or phases along the grain boundaries.

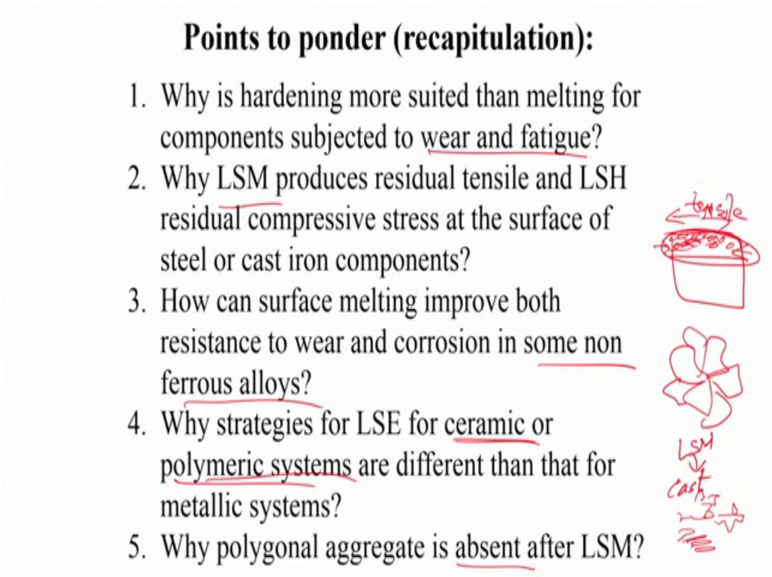
So, as a result these grain boundaries are decorated with compounds which are extremely resistant to chemical attack. So, these regions now act as cathodic. So, they are they are highly cathodic meaning they do not want to dissolve whereas, the core is highly anodic. So, you easily create a core which is anodic and a surface which is cathodic. So, as a result of which you actually will have a situation that there will be easy oxidation of this core and because of this oxidation possibility. So, you will create an galvanic cell between these two regions of the microstructure and there will be easy corrosion happening. So, there will be dissolution of cations from the core and the material will undergo heavy amount of degradation.

Also this kind of a microstructure will mean that these regions will be harder and more wear resistant than the core. So, again during a relative motion these portions will undergo more of wear than the surface that the grain surfaces. So, if we simply by surface melting and rapid solidification following the laser surface melting. If we can convert this kind of a microstructure into ultra fine microstructure like this. We were able to demonstrate that it improves it gives you two fold benefit. One is improvement because of grain refinement and uniform distribution of these inter metallic phases the hardness and the wear resistance improves.

And on the other hand another very important advantage is that from this microstructure when you create very small crystallite size where the distance between the core and the surface is so small that you cannot create a potential galvanic cell between analytic and cathodic part. So, in other words if this cathodic components get distributed all over so there is no easy formation of any galvanic cell into the microstructure. So, the corrosion property also improves.

So, you get two fold improvement of wear resistance and corrosion resistance. And, this strategy is applicable not just in magnesium alloys bearing certain rare earth elements can be true for all other non-ferrous systems which can be given a very limited surface melting up to a certain depth leading to ultra fine grain refinement which in turn will give you very high wear resistance and also a corrosion resistance. I mean this is not the universally possible, but certainly possible and can be extended to very many systems or non ferrous systems where martensitic transformation is not possibility.

(Refer Slide Time: 24:07)



Points to ponder (recapitulation):

1. Why is hardening more suited than melting for components subjected to wear and fatigue?
2. Why LSM produces residual tensile and LSH residual compressive stress at the surface of steel or cast iron components?
3. How can surface melting improve both resistance to wear and corrosion in some non ferrous alloys?
4. Why strategies for LSE for ceramic or polymeric systems are different than that for metallic systems?
5. Why polygonal aggregate is absent after LSM?

So, let us try and summarize what we have discussed is that hardening as a strategy is more I mean hardening without melting as a strategy is more applicable to steel because it produces not only martensite predominantly martensitic microstructure, but also residual compressive stress which is beneficial to improve both resistance to wear and fatigue. Surface melting produces residual tensile stress because what happens is if you have a component and this is the surface. So, when it melts it actually expands and then when it tries to solidify. So, there will be a possibility there will be a tendency of shrinkage.

So, tendency of shrinkage means this layer will tend to shrink in the process the reaction to that tendency will be a tendency of residual stress which is acting away from each other. So, tensile in nature So, this kind of a situation is not desirable, but in other words if you do only surface melting then this is the kind of a scenario that you develop onto the surface.

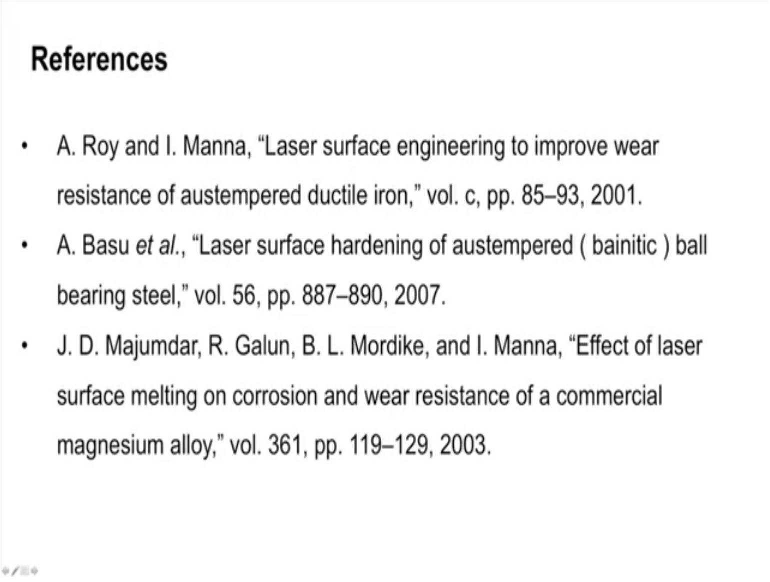
But in case of steel you would rather you can avoid this because of the possibility of martensitic transformation, but in case of non ferrous systems still you adopt surface melting as a strategy because it gives you another kind of a dividend another advantage and that is very small ultra fine, grain size or grain refinement. And, this kind of grain refinement actually is beneficial.

So, this is what we actually demonstrated in case of magnesium alloy, but it can be useful to other non ferrous systems as well. In case of ceramic and polymeric materials these approaches do not actually work that is purely because we are either dealing written on crystalline systems like in polymeric systems. Or in ceramic systems the melting temperatures are so high that if you try to melt the surface you end up actually damaging the phasing degrade. They may degrade they may undergo some dissociation and that can create a permanent dimensional change or even formation of crack.

Because the temperature that you have to heat up to it will be several 1000 degrees centigrade and subsequent cooling will be where can create a lot of thermal shock. So, they are they are not amenable to laser surface hardening or melting that kind of a surface treatment. But you can certainly create certain groups, certain surface patterns for creating surface texture or even in polymeric systems of course, you can allow controlled crystallization or certain other annealing effects and so on.

But by and large these surface hardening, surface melting all these techniques are more suitable for metallic alloys. In case of surface melting of metallic components like the way I was showing in case of magnesium alloys. Usually you do not necessarily develop a nice polygonal microstructure. So, this is difficult to develop by surface melting that is because my surface melting when you do laser surface melting what you develop is a cast microstructure. So, they are highly inhomogeneous and necessarily you may see some dendritic patterns, but not complete polygonal shape. So, this dendritic pattern will show up or maybe directionally solidified grains, but not really polygonal microstructure. So, so this is the absent after surface melting.

(Refer Slide Time: 28:11)



References

- A. Roy and I. Manna, “Laser surface engineering to improve wear resistance of austempered ductile iron,” vol. c, pp. 85–93, 2001.
- A. Basu *et al.*, “Laser surface hardening of austempered (bainitic) ball bearing steel,” vol. 56, pp. 887–890, 2007.
- J. D. Majumdar, R. Galun, B. L. Mordike, and I. Manna, “Effect of laser surface melting on corrosion and wear resistance of a commercial magnesium alloy,” vol. 361, pp. 119–129, 2003.

I think with this we will stop here and what we have discussed so far is only changes associated with microstructural changes. So, whatever improvement in properties we could discuss was all because of changes in microstructure. In the next lecture we will talk about changing my composition, both composition microstructure and see how much more we can achieve in terms of surface engineering.

Thank you very much.