

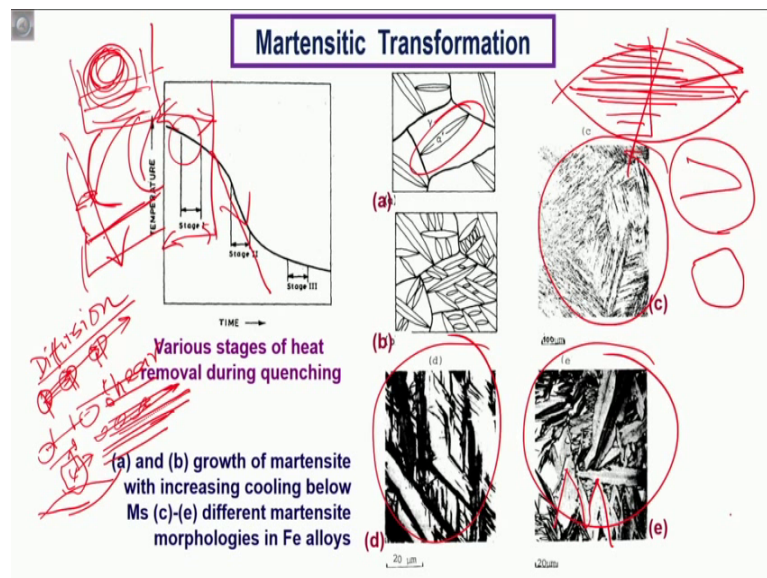
Surface Engineering for Corrosion and Wear Resistance Application
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Lecture – 21
Non Diffusive transformation in Steel

So, welcome to the 21st lecture of Surface Engineering. In the previous lecture we discussed two very important types of transformation products in steel, namely the pearlitic and bainitic transformations, both of them arising out of eutectoid transformation, only the phase aggregate the product aggregate is different in these 2 cases and that is and also they followed 2 different transformation mechanisms. But, today we are going to talk about martensitic transformation, which is very different in terms of mechanism, product morphology and the path taken.

And, the basic difference arises from the fact that, martensite is a non diffusion control transformation product or so called shear transformation product, as against diffusion control transformations of the other varieties of pearlitic and bainitic transformation.

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So, let me just clarify this part right away, that when we talk of a diffusion controlled then, what we mean is that in a given lattice, if we have atoms which are located in certain positions like this, when the atoms move they move from one designated position to the next and then.

So, exactly the distance of separation from one jump or the length at which an atom will jump from one to another position, will be exactly the multiple of inter atomic distances, when we talk of shear, then the 2 neighbouring atoms, when there is a migration, the migration will not be exactly up to the next position of the atom. So, it will be rather in the somewhat in between. So, the distance of separation will not be integral but, fraction of inter atomic distances. So, when we talk of diffusion, then we are talking about migration by inter atomic distances, exactly inter atomic distances, in a given crystallographic directions on a given plane.

Similar thing, when we are talking about shear then, we are talking about migration of atoms, from one position to the next, which is not in exactly a distance equal to the inter atomic distances but, a fraction of that and this happens because, of certain other reasons and under certain other compulsions, which we will discuss later. But, a another important part that I would like to tell you is that for example, when we talked about TTT and the CCT diagrams and in the TTT or CCT diagrams we said that if this is the. So, called TTT diagram, the corresponding CCT would be somewhat like this.

And we said in order to avoid in order to get martensite, which is the this is the martensite start line let us say. So, in order to hit this line without intersecting the pearlite start or bainite start and finish, we need to employ a very fast cooling rate and this gap since, it is less than a second for plain carbon steel, we actually need to employ a very drastic quenching. So, whenever you actually quench a hot steel component, into some bath containing some fluid so, that you can extract heat faster.

We would like to avoid this zone. So, whenever we drop a hot body into a certain fluid, there will be immediate formation of vapor blanket around and that will hit out the heat transfer and this is what is going to happen in the 1st stage. So, during the quenching process, we would like to minimize this 1st stage as low as possible and would like to employ the 2nd stage, as much as possible. So, that the heat transfer is the fastest and uniformed during this stage. Now, when we talk of martensite, we need to understand that here, the product is not going to form in equiaxed shape like growth in all directions to the same extent, this will not happen in case of martensite.

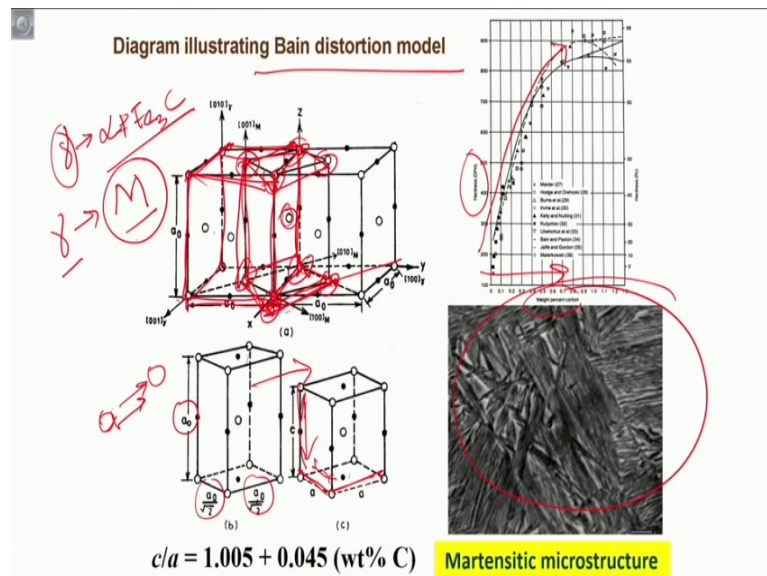
Since, it is a process dictated by shear and shear of set of atoms in a given direction, only by fraction of inter atomic distances. So, if that shear happens in this particular plane,

another shear happens in another plane another. So, these are all parallel crystallographic planes and when the shear happens in them, the degree of shear is going to be different and as a result of which the morphology or the shape of the product that we develop, will be more like a lenticular shape. That is because typically we may say that, if this is the mid plane, if this is the mid plane and if the shear is happening to different this to different extent, as we go from bottom to the top.

And also happening similar things below the dividing plane then, the overall shape of the product will look like a lens or a lenticular shape and a half of it, will appear as a little shape. So, needle or a sphere shape so, this needle or sphere shape is typical of martensite, as opposed to the polygonal shape of any other division control transformation product. So, this is the kind of a shape is what we always expect.

And typical microstructure these are real these are all sketches but, this is a real time microstructure in steel, plain carbon steel, this is in alloy steel and this is an iron nickel system where, we actually happen to see a morphology, which clearly tells us there is a very large influence of orientation present influence of orientation, for the growth of these kind of martensitic plates.

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So, we if we move on, we also need to understand that where is this martensite coming from. So, for example, the initial reactant is austenite, which is interstitial solid solution

of carbon in gamma iron, FCC iron and this in case of pearlite, we would have or bainite, we would have expected ferrite and cementite to form as a 2 phase aggregate.

In case of martensite, what we expect is a product, which is either phase centered, body centered tetragonal or low tetragonal decubic system. So, the crystal structure changes, without any change in composition. So, if you initially are dealing with FCC cement FCC austenite.

So, this is the contour of such an FCC unit cell and in this FCC unit cell, what you have will be the 6 atoms at the 6 phase centering positions and 8 atoms at the 8 corners. So, you have 4 effective number of atoms per unit cell but, now if this crystal structure of this unit cell because, of very large compulsion and no time given, suddenly changes or is forced to change into and take up a new crystal unit cell.

The possibility exists whereby, you now have to consider these 4 atoms on the top plane, these 4 atoms at the bottom plane and one more at the center which earlier was the phase centering position. So, now, we are looking at formation of a new unit cell, out of the existing FCC unit cells. So, 2 neighboring FCC unit cells, from the 2 neighboring once we have squeezed out a new unit cell, whereby the length here, is exactly the same as the length in this direction, this direction.

So, the length is exactly a naught but, on the other 2 directions, the lengths are now shortened, squeezed by an amount of a naught over root 2 because, this length is you can easily calculate that this length will be root 2 a and half of that, will be just a upon root 2.

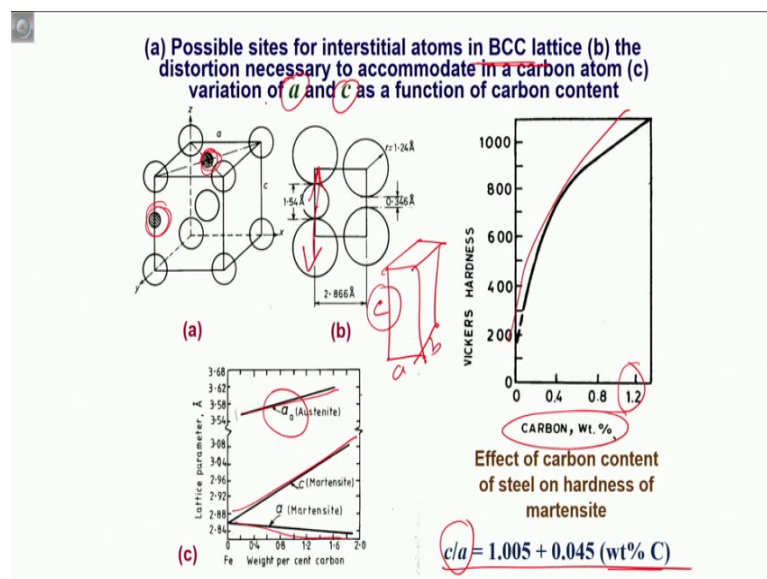
So, this means that earlier an FCC unit cell where, a where a b and c, where all equal and we had 4 (Refer Time: 09:25) atoms per unit cell is now, transformed into your new unit cell, which has 1, 2, 3, 4, and 5, 6, 7, 8. So, 8 atoms at 8 corners but, so, effective number is only 1 and 1 in the center of the unit cell. So, another so, 2 per unit cell but, the difference is that this axial length is different than the 2 other axial, 2 other axis. So, the from this part, the product what actually emerges is going to be a tetragonal unit cell because, a is equal to a. So, in x and y direction they are equal but, in z direction they are different.

So, a is equal to a but, not equal to c and this is possible, if we assume that as if the entire transformation is happening due to some readjustment of such a change in crystal

structure from FCC into a body centered tetragonal but, this is hypothetical. In reality, this kind of a Bain distortion model is not valid but, good enough for us to understand as to how tetragonal crystal lattice can emerge from existing phase centered cubic lattice, without necessitating any large scale rearrangement of atoms except that the atoms need to just move by fraction of inter atomic distances, from one position to the next and allow such new unit cell to emerge.

So, this is the overall microstructure, these are real time microstructure and one other thing what we should know is that the amount of carbon is very important in developing such tetragonality. For example, here it is manifested in terms of a surface dependent property called hardness, as a function of carbon. So, if we increase the amount of carbon, the hardness of the steel, increases and that is purely because, the super saturation in martensite increases, with more and more addition of carbon.

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In fact, the distortion that we were talking about now, is better understood here. So, typically in a BCC lattice which is what you expect at room temperature. So, FCC tries to transform to BCC but, the carbon which has the option of going either into this phase centering position of the BCC unit cell or middle of the edges. So, this would have octahedral coordination and the this would have a tetrahedral coordination. So, if it chooses either of these positions for example, if it goes to the middle of the edges, then we see there is immediate lattice expansion in this direction.

So, it is exactly because of this reason, in a tetragonal unit cell where, you expect that the c direction to be larger than the a and b direction. So, this tetragonality or deviation from the cubic geometry is going to be larger, if the amount of carbon is more. So in fact, that is exactly what we see, that as we increase the amount of carbon the hardness of steel, which is coming from martensite increases and this is felt until about a certain limit of addition of carbon.

So, this is an empirical relationship which actually says, that if you increase the amount of carbon that tetragonality the c over a ratio increases and because of which the hardness increases. But, when you actually pump in more or dissolve more amount of carbon, it is not only that at a terminal martensite but, even in austenite which is the parent phase where from martensite actually forms. Even in austenite the lattice parameter increases and so, does in case of the c axis of the tetragonal martensite but, you see a certain amount of contraction. So, that is what we saw already in our previous slide, in the Bain distortion model, that the c axis expands whereas, the a and these 2 axis they contract.

So, carbon plays a very important role, in defining the tetragonality of martensite, in terms of these 2 lattice constants and eventually that determines the overall mechanical property of martensite, we also have understood that this is a process whereby no large scale solute partitioning takes place.

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Martensitic Transformation – Characteristic Features 1

- Named 'Martens', it is the hardest solid solution phase in steel
- Martensite is not always hard, e.g. thermo-elastic Fe-Ni martensite is soft. Martensite occurs in non-ferrous systems, too.
- The transformation is displacive or shear type involving no long range diffusion, hence non-isothermal (mostly) or athermal in nature.
- Martensitic change occurs in pure metals (Ti, Co), alloys (steel, cast iron, stainless steel, Fe-Ni-C, Fe-Mn-Si-(Cu-Al, Fe-Pt, Ti-Ni, Au-Cd), ceramics (ZrO₂), minerals, solidified gases (Ar-40N₂), inorganic compounds, even polymers
- Diffusion-less process, occurs usually at low T where diffusion coefficient is low and thermally activated migration is unlikely
- Crystal structure changes, no change in composition (similar to allotropic/polymorphic and massive)
- Heterogeneous nucleation occurs at grain boundary, martensite plate itself. Nucleation barrier is low due to low interfacial energy
- Martensite plates, laths or needles, are always confined within the parent grain – never grows beyond grain boundary or other martensite plates. GBs act as barrier for coherent interface to grow beyond

1061K

α 0085

Fe₃C

65%

(8) (17)

And transformation is through shear, which essentially requires the atoms to move only by fraction of inter atomic distances and not by integral multiple of inter atomic distances. So, now actually I decided to make a summary for you to follow the martensitic transformation in the nutshell. So, first of all the name martensite comes from the German scientist, mark metallurgist who actually first proposed the existence of martensite in steel because of a fast quenching.

So, it is the hardest solid solution phase possible in steel, we are talking about not the hard not the hardest phase but, hardest solid solution phase because, the hardest phase in iron carbon system is the interstitial compound called cementite. So, martensite is usually hard and in fact, it is because of this strength we always are so much interested in martensite but, there is no necessity that martensite always have to be hard.

For example, if you go to iron nickel system or titanium nickel system, the martensite that forms are called thermo elastic martensites and they are actually in a strange condition they are not necessarily very hard. They the strength of those martensites arise because of those alloys arise because, of another phenomenon, which follows the transformation and that is precipitation hardening. Now, martensite again is not necessarily occurring only in steel, it can occur in very many non ferrous systems.

In fact, I have listed a large number of systems here, these are ferrous systems but, you see martensite can also arise in many other alloys which are not necessarily steel, which are non ferrous alloys, it can happen even in non metallic systems for example, in zirconia which is an oxide, it can happen in various minerals, solidified gases at ultra low temperature, in inorganic various, inorganic compounds and even in polymers.

So, though we often tend to believe that martensite is almost the prerogative of steel but, that is not true. So, what is important for us to know is that martensite is a product of a transformation of a particular mechanism of transformation and is a generic name, not only confined to steel; it can happen in other systems as well.

But, in the surface engineering course, the reason why we are discussing so much about martensite or pearlite and bainite is because, a large number of components, large number of bodies, large number of engineering applications are based on steel and when we want to improve upon their life or their performance, we do carry out certain

transformations onto the surface, which imply exactly the same type of phase transformations that we are discussing so far.

But, the most important thing in case of martensite transformation is the nature which is diffusion less; that means, the atoms move not by integral multiple of distances but, by fraction of inter atomic distances, it happens at very low temperature, where diffusion is very low. In fact, that is one of the reason why for example, when you quench all the way from 800 to room temperature, the diffusion coefficient actually decreases by orders of magnitude.

And at room temperature or sub below room temperature the diffusion coefficient is so low, that it will take years for any transformation, which is possible at high temperature to happen at room temperature. So, there is no thermally activated migration involved and atomic transport is purely by shear and which again I must reemphasize is by a fraction of inter atomic distances.

Another very important feature is that there is no change in composition. So, when you talk of pearlite or bainite, you start with austenite and there is immediate solute separation. So, that 2 different phases formed like ferrite and cementite, ferrite would typically contain a carbon to the tune of 0.258 percent carbon whereas, cementite will have 6.67 weight percent carbon. So, from about let us say, if you are dealing with a 0.4 or 0.6 percent carbon steel, which is what will austenite contain. So, point points from 0.6 percent carbon, you swing all the way 2 different phases of alpha and Fe₃C.

Which if this contains let us say 0.6 percent carbon so, you are now talking about a phase compositional variation as large as this, in case of martensite, there is no such phase, no such solute segregation or solid separation. So, whatever carbon you have in gamma will be retained in martensite, in other words you actually produce a highly supersaturated solid solution, we will come to that as to why martensite is so hard.

This is this kind of a transformation where crystal structure changes but, composition does not change is very similar to the allotropic or polymorphic changes or even massive transformations. But, here all these again the point of distinction is that allotropy or polymorphism or massive these are diffusion control transformations whereas, martensite is a shear transformation product. Martensite is also a heterogeneous process so,

nucleation occurs typically at grain boundaries or different martensite plates or even dislocation tangles and so on.

But, nucleation barrier is very very low and also the interfacial energy is very low. So, nucleation so, typically in any nucleation process, when we talk of this barrier, this barrier in case of martensite is very very small because, the interface actually is of very low energy. So, martensite can actually form in the can actually manifested in the form of plates, laths or needles, I am sorry there is a spelling mistake here, then it can be but, it is always confined within the parent grain, which is a parent grain of austenite.

So, if this is the parent austenite grain and if martensite plate forms, it can go all the way up to the boundary but, never crosses and moves to the other crystallite, across the boundary.

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Martensitic Transformation - Characteristic Features 2

- Martensite morphology is mainly lenticular or lath type. Also possible: butterfly, plate type, mid rib, etc
- Martensite is hard due to supersaturation, small grain/plate size, bcc structure, internal strain, high dislocation density, poor slip system
- Transformation is irreversible with a hysteresis in Fe-C (steel) system but completely reversible in Ti-Ni, Fe-Mn and other systems
- Reversible both in terms of direction of transformation, shape and site of nucleation. However, a temperature hysteresis may exist between M_s and A_s (martensite (cooling) and austenite (heating) start)
- Reaction growth velocity is extremely rapid: close to velocity of sound, takes $< 10^{-7}$ s per plate to grow.
- Transformation begins at M_s and completes at M_f (on cooling). Transformation rarely goes to 100% due to accumulation of stress
- Reaction front is a coherent glissile interface (typical of martensite)
- M_s may be raised to M_0 by prior deformation. Application of external stress or resultant strain may activate some new growth variant
- Similarly A_s may be lowered by prior deformation or external stress
- Transformation hysteresis may be large (Fe-C) or small (Ni-Ti)

Handwritten annotations:
 - A diagram of a lenticular shape with arrows indicating transformation directions.
 - The phrase "Shape memory" written in red.
 - Red circles and lines highlighting specific terms and values in the text.

Now, the morphology usually as I said is of lenticular shape. So, typically you would expect a lens like shape and if you see the half of it or take your section is such that you are viewing at a different angle. So, you tend to see such needle like or sphere like structure.

But, you also can have instead of lenticular or lath type, you can also see butterfly or plate type or midrib structures and so on in, primarily in non ferrous systems. Martensite is the hardest solid solution because of very many reasons, most important is the super

saturation, higher the amount of carbon, greater the super saturation and greater is the strength. Also because, it has very small plate size, I would rather not use the term grain because, we are not talking about polygonal shape, we are talking about large aspect ratio, lenticular or plate or sphere like shape.

So, very small plate size, the crystal structure is BCT, which is certainly less plastic and hence, less number of slip systems available, compared to the parent austenite or which has an FCC. There is lot of internal strain involved because, of the contraction and expansion in 2 different directions, martensite contains a large density of dislocations because of the large stresses created during the transformation and you are very few are very poor slip systems. So, all these are important reasons as to why martensite is the hardest solid solution?

The transformation is irreversible because, you know unlike; in case of say pearlite, where you actually go to ferrite and cementite combination. But, when you reheat you get back the austenite, in case of martensite, austenite transforms to martensite but, when you reheat martensite, you do not necessarily get back austenite, you actually martensite dissociates into pearlite, which is ferrite plus cementite and then if you reheat, then you go back into austenite. So, this is not directly reversible transformations.

But, in some other systems, they can be completely reversible; for example, titanium nickel are a nickel and it is because of this reasons, these classes of alloys, typically show the phenomenon called shape memory, which is totally absent in case of steel. Now, the transformation occurs basically below a temperature called martensite start. Now, typically if you again refer to the CCT diagram now, let us refer to the CCT diagram. So, you will see there at an M_s martensite start and M_f which is martensite finish transformation, which are just lines and not curves they are lines.

Because, martensite is a thermal transformation, it is not a temperature depend, it is a temperature dependent but, it is not thermally activated process. So, you require so much of driving force, in terms of under cooling but, once you start, even if you hold here for a infinite time, the volume fraction of the phase will not change. The volume fraction of phase of martensitic product, will change only when you go to lower and lower temperature; that means, when you increase the driving force, in terms of under cooling.

In case of diffusion control transformations, we all know that, if we hold at an isothermal condition, the product volume fraction increases with time. So, that is a time dependent transformation, martensite being an a thermal process is a time independent transformation. We must know that martensite actually is a very rare transformation, which occurs at very high speed almost at the speed of a propagation of sound but, with a coherent glacial interface.

We did talk about role of crystal defects and generally we found we did discuss at that point of time, that an if an interface is coherent then, the mobility is generally very low but, here we are seeing a very rare combination, where we are saying that the interface is coherent and yet highly glacial. So, much so, that it can move at a pace which is almost equal to the velocity of sound, the temperature the so, called M_s and M_f temperatures, can be raised to slightly higher level by applying plier deformation.

And then the start temperature is called martensite deformation martensite transformation start by prior deformation. So, M_d is a raised level of M_s by way of because, of prior deformation because, these prior deformations produce lot of dislocations, which act as nucleation sites for modern sites. So, hence even with slightly lower under cooling means, normally you require. So, much under cooling but, even with slightly lower under cooling now, martensite can start nucleating because of the presence of large density of dislocations, due to prior deformation.

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Martensitic Transformation – Characteristic Features 3

- The extent (volume fraction) and plate size of martensite can be controlled by the extent of cooling or heating within M_s and M_f – thermoelastic or rubber like behavior – in some systems
- Growth occurs by cooperative shear displacement of atoms by fraction of interatomic distances (displacement being proportional to distance from initiation site, matrix-product interface) with a planar coherent interface
- Transformation occurs on invariant or habit plane of parent matrix and martensite plate bears some orientation relationship between product and parent phase: e.g. (i) In Fe-30Ni: (fcc to bcc) $(111)_A \parallel (011)_M$ and $[-1-12]_A \parallel [011]_M$ on $(259)_A$ habit plane; (ii) In steel: (fcc to bcc) $(111)_A \parallel (011)_M$ and $[-101]_A \parallel [-1-1-1]_M$, on $(225)_A$ habit plane
- Interface maintains continuity across parent-product phase
- Transformation occurs with lattice invariant deformation leading to invariant plane strain - slipping or twinning
- In non-ferrous systems, invariant plane strain creates stacking faults
- Driving force: mostly chemical $\Delta G_m < \Delta G_f$ at $T < T_0$

Now, we generally the volume fraction and the plate size of martensite, you can control by the extent of cooling or heating and. In fact, in some other systems, actually they can behave completely reversibly so, called thermoelastic or rubber like nature but, this is not in steel but, in some other non ferrous systems. I already mentioned and let me repeat that the growth occurs by cooperative shear displacement.

So, essentially if one plate moves this much another plate moves this much, another this much, another this much. So, until the mid plane, the degree of shear varies, in other words from the mid plane as you grow up or away from the central plane, the degree of shear actually decreases and as a result, we end up seeing such lenticular shape. So, that this lenticular shape develops because of that.

Now, when the transformation takes place, actually there are one can define a certain reference plane called the invariant or the habit plane, where martensite usually nucleates. Now, if you compare with the plastic deformation, we always say that dislocations are prone to move or finds it easy to move, in slip systems comprising closely packed and loosely stacked. So, essentially we are talking about planes, which are wide apart but, very closely packed. So, the atoms should almost touch each other.

In case of martensite, we see just the reverse, remember for diffusional transformations, we require closely packed and loosely stacked planes. In case of martensite, we actually require, atoms which are rather widely rather wide that slightly wide apart but, very close by the planes are very close by. So, just the opposite for martensitic transformation, we require wide apart bus but, closely packed planes.

And these kind of planes, these kind of restriction actually brings us to the possibility of seeing this transformation occurring on some specific types of planes called habit planes, which is this described here. For example, in iron 30 nickel alloy or in typically in steel or in some other alloys, there will be certain planes where such kind of transformation or martensitic transformation is favored and that is purely arising out of the fact that for shear is actually require atoms slightly apart. So, that the atoms can move by a fraction of inter atomic distances and not hop from one place to the very next possible position.

The this invariant deformation that happens in case of martensite transformation, leads to invariant plane strain and there is of course, there is no slipping but, there could be this

can lead to formation of certain amount of quench. So, it is quite commonplace that certain martensites actually would be largely twin martensite.

In case of a non ferrous systems, this invariant plane strain can create stacking faults. So, that is also a sort of crystallographic defects, which further makes a deformation or deformability difficult and in the process increasing that increases the strength. The most important point at part that we must remember, that entire driving force for martensity transformation primarily comes from which is primarily is of chemical nature which, essentially means that if this is the austenite we are talking about and if this is a eutectoid point when, we quench all the way to very low temperature.

So, this is in terms of the phase diagram and in terms of the kinetic diagram, if we are if this is the austenite start and if you are quenching all the way from way above austenite start and quenching way below.

Then this large ΔT is proportional to a very large super saturation and this is exactly the driving force for martensitic transformation. So, when you make life so difficult that, you are quenching all the way from above 800 to room temperature or below, in this very large decrease in temperature quenching, you are not allowing any time at all for diffusion to take place.

So, there is no pearlite, no bainite and then the solution austenite has to transform because, it is highly metastable because of this very large under cooling and the only way it can now transform is by shear, by a fraction of inter atomic distance movement. And not by diffusion control transformation where, atoms move by integral multiple of inter atomic distances.

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Points to ponder (recapitulation):

1. What is martensite? Why is martensite not found in Fe-Fe₃C phase diagram?
2. Why is martensite the hardest solid solution?
3. How is growth of martensite different from that of pearlite or bainite?
4. How is martensite relevant to surface engineering of steel components?
5. Is martensite always hard? Can it acquire different shape? Is it found only in steel?
6. Would you desire and design a surface with 100% martensite?

So, it is time to recapitulate. So, in this last half an hour or so, we have discussed only about martensite and of course, at times compared with pearlite and bainite, I think by now it is clear to you that the martensite is a shear transformation product, where atoms moved by fraction of inter atomic distances, retains the entire super saturation, the entire amount of carbon that you had in austenite.

You need drastic quenching. So, that you do not allow any diffusional transformation like paralytic or benedict to intervene and weaken or reduce the super saturation, we discuss as to what are the other possible reasons like, a lack of slip systems or relatively complex crystal structure like, body centered tetragonal, a very small size of the plates or the platelets and so on because of all these reasons we see martensite as the hardest solid solution.

The growth mechanism is completely different compared to pearlitic bainitic can for that matter any other diffusion control transformation including allotropy or a massive transformations and so on, why is martensite relevant to surface engineering at all? It is purely because, very soon we will start discussing about various techniques for surface hardening and then whenever we talk of surface hardening of steel, we will definitely invoke the concept of formation of martensite onto the surface.

And we would rather like to create a situation, where we transform the austenite, we heat the surface to austenitic state, make it austenite and then subsequently by rapid

quenching onto the surface, we convert the surface into martensite but, not the core. So, with the core can very well be retained by pearlites. So, that the toughness is retained and the ability to absorb energy is retained but, the surface becomes predominantly martensite. So, that it can withstand or resist a wear or any other kinds of degradation.

And we talked of briefly, we alluded to various possibilities of martensite being non hard or not as hard as in steel and that is typically in case of a non ferrous systems and we also found out that martensitic transformation or this shear type of transformation and as a generic mode of transformation is possible in very many systems, even in nonmetals solidified gas, ceramics oxides, even in some polymers. But, finally one question that we should ask ourselves that if martensite is so good and so beneficial, would we care to have 100 percent martensite in the bulk or on the surface.

The answer is no, the answer is no and you have to find out as to why 100 percent martensite is not desirable and I can give you an only one hint that though martensite is very hard, martensite also is brittle. So, it cannot absorb energy and hence it can lead to easy formation of cracks.

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So, thank you very much.