Steel Making

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Steelmaking, Additional Topics

We continue our discussion on clean steel. We have seen various aspects of clean steel and its relationship with the inclusions. Now, not all sizes of inclusions are harmful. In fact, the size of the inclusion, which can be tolerated, will depend upon the particular application; that means, there is a critical size below which the inclusions are harmless, but above which they will be harmful.

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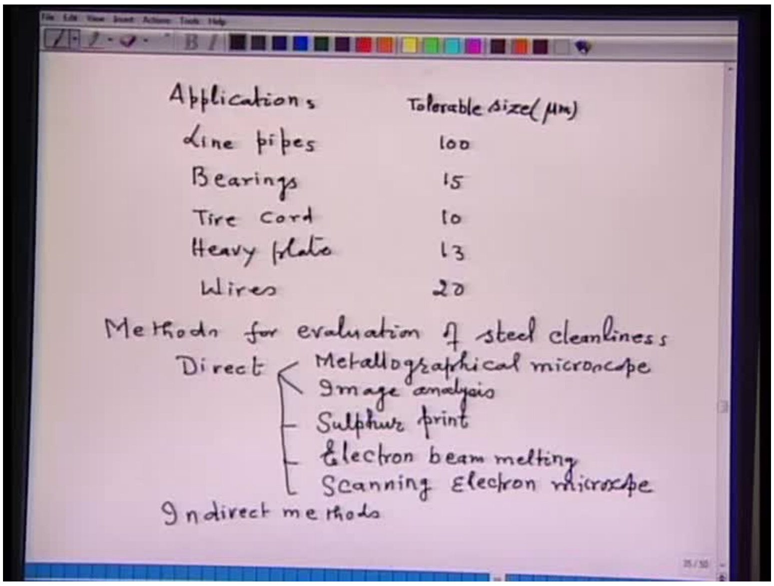

Applications	Tolerable size (μm)
Line pipes	100
Bearings	15
Tire cord	10
Heavy plate	13
Wires	20

Methods for evaluation of steel cleanliness

Direct
- Metallographical microscope
- Image analysis
- Sulphur print
- Electron beam melting
- Scanning Electron microscope

Indirect methods

I will give with some applications and the tolerable size. For example, steel for line pipes, the tolerable size is 100 micron meter; then, for bearings, the tolerable size is 15 micron meter; then, tire cord, 10 micron meter; heavy plate, 13 micron meter and wires, around 20 micron meter. So, these are the critical sizes. There could be several other applications, which can tolerate some minimum size. Hence, the size above that should be removed, but below that if it remains in the steel, it does not harm the property.

Now, the impact property will depend upon whether inclusion is brittle or ductile. Low deformability affects hot working, because if the inclusion is non-deformable, then during deformation processing, it will break because load is applied. As such, macro inclusions are harmful. Inclusions that have lower coefficient or thermal expansion, then matrix set up stresses in the matrix and cause fatigue failure. These effects we have already seen in our previous lecture.

Now, methods for evaluation of steel cleanliness; there are several methods through which one can assess the number, size and size distribution of inclusions. First method is… I will classify them: direct method and indirect method. Among the direct method, one is metallographical microscope; that means take a specimen, polish it and it is seen under the microscope. The microscope analysis can tell the number, size and size distribution of inclusions.

Another important is the image analysis. Now, packages and softwares are available, which can analyze the image for the inclusions. Third method is sulphur print. Sulphur printing is taken and one can also see what the inclusion is over there. Still another method is electron beam melting. In the electron beam melting, sample is melted under vacuum by electron beam and inclusion throughout; from there, one can find out what is that inclusion. Another steel direct method is scanning electron microscope. In this particular method, the importance is sample preparation and sample can be seen under the scanning electron microscope; the image can be analyzed for the size, type and size distribution of inclusions.

Another method; they are called indirect methods. In the indirect methods, one can determine total oxygen. From the total oxygen and the presence of oxide forming element, one can determine the approximate number of inclusions. Also, one can do nitrogen determination and from there one can determine the number of inclusions. So, these are the methods for evaluation of steel cleanliness.

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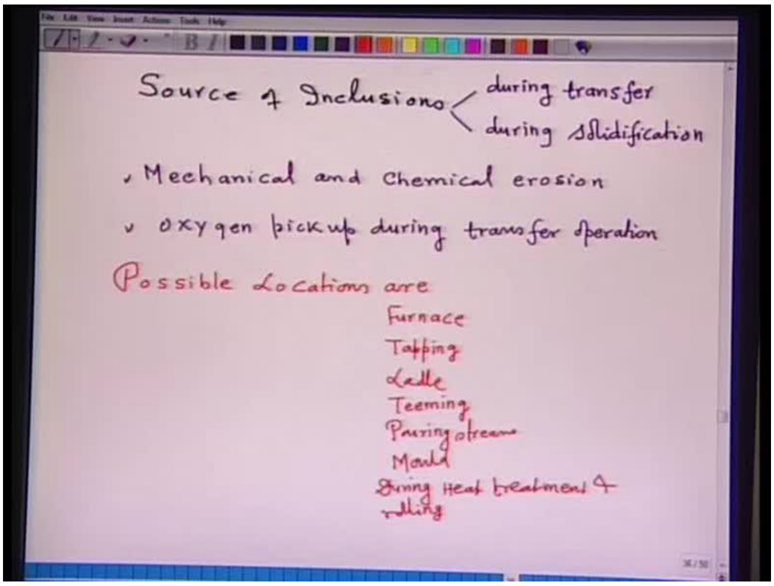

Source of Inclusions
- during transfer
- during solidification

- Mechanical and Chemical erosion
- oxygen pickup during transfer operation

Possible Locations are
- Furnace
- Tapping
- Ladle
- Teeming
- Pouring stream
- Mould
- During Heat treatment & rolling

Now, it is important to know the sources of inclusion. What are the sources of inclusion? Now, here it is to be noted that inclusion does not form in BOF steel making; that is, during conversion of hot metal to steel, inclusion in BOF converter do not form. Equally, they do not form in electric arc furnace steel making; equally, they also do not form in energy optimizing furnace. So, the formation of inclusions occurs at two sources. One – during transfer of molten steel from one vessel to another vessel; for example, when BOF steel or electric arc furnace steel or EOF steel is tapped, then a tapping stream is a source, where atmospheric oxygen can be entrained and it can cause inclusion formation. Then, from ladle, it goes to secondary metal processing operation; then from the secondary metal processed steel, which is again contained in the ladle, is transferred to the tundish. So, during the various transfer operations that takes place between the tapping of heat from the primary vessel, which is either BOF or EAF or EOF and to the casting stage. So, several transfer operations occur under the atmosphere, which causes oxidation and hence, the formation of inclusions.

Another source of inclusion is during solidification, because when steel solidifies, then the impurities are rejected into the liquid, because of the low solubility of that impurity in the solid. So, accordingly depending on the concentration of impurity and depending on the partitioning of solute element between solid and liquid, the formation of inclusion does occur during solidification of steel. In fact, during solidification, it occurs, which is called precipitation due to reaction from molten steel or during solidification. Another source of inclusion is that right from BOF to continuous casting or ingot casting, the molten steel is contained in the refectory lined vessel. So, the mechanical and chemical erosion of refectory will also lead to formation of inclusion. Then, as I already said, oxygen pickup during transfer operation.

Now, if you want to identify the location, then possible locations are furnace tapping; that is, so-called tapping stream. Then, ladle teeming; that is, the teeming stream. Then, pouring stream, then mould; also, they can occur during heat treatment and rolling operation. So, these are the subsequent locations, where molten steel is handled; except in the last stage during heat treatment and rolling, where solid steel is reheated to around 1200 degree Celsius to create the different properties, there also, the oxidation can occur. Hence, some sort of inclusion formation can take place. During solidification, the inclusions, which are likely to form, will depend upon the concentration of the impurity and the partition coefficient of that impurity. Normally, oxides, oxysulphides, nitrites, carbonitrides can form during solidification.

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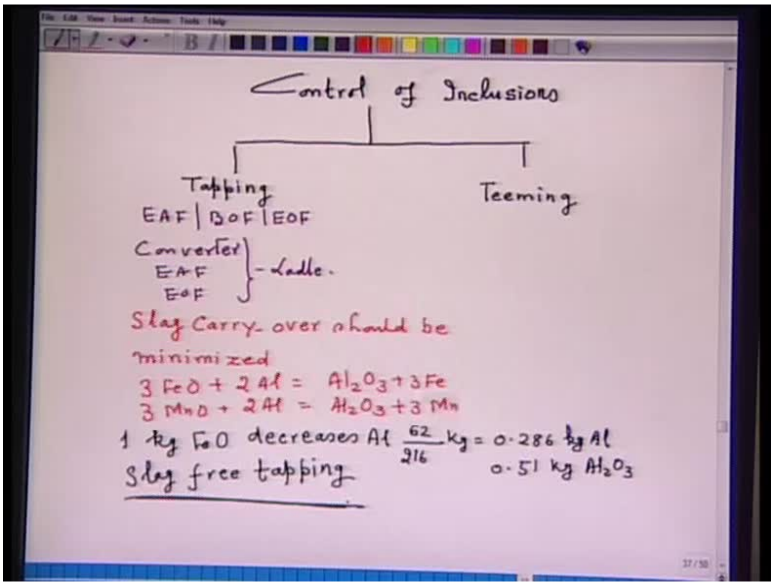

Control of Inclusions

Tapping

EAF | BOF | EOF

Converter
EAF
EOF
} - Ladle.

Slag Carry-over should be minimized

$3\,FeO + 2\,Al = Al_2O_3 + 3\,Fe$

$3\,MnO + 2\,Al = Al_2O_3 + 3\,Mn$

1 kg FeO decreases Al $\frac{62}{216}$ kg = 0.286 kg Al

0.51 kg Al_2O_3

Slag free tapping

Teeming

Once you know these are the sources of inclusion, then how to control the inclusion formation? Obviously, the next thing, which is important, is control of inclusions. Now, a clue for control of inclusion will come from source of inclusion; that is, from where the inclusion comes, you control it. So, inclusion will not be entering or will not be forming during the subsequent stages. So, as such, what will I do? I will try to make a flow sheet to explain the control of inclusion; say one source we have seen tapping; I will put the control of inclusion can be done during tapping. Also, it can be done during teeming. So, you have seen that tapping and teeming are the two operations that are carried out between primary steel making unit and the casting unit. So, in between, several operations are going on, which lead to the formation of inclusions.

Let us see first about the tapping. Now, tapping from either EAF, electric arc furnace or BOF or EOF; I can also include these in my lecture. From tapping, steel goes from converter; or from electric arc furnace or from EOF, it goes to ladle. What happens during tapping? During tapping, what can happen is the slag carry-over should be minimized, because whether converter or EAF or EOF, whatever the steel unit be, the steel is covered by a slag. So, during tapping… The carry over slag should be minimized, why? Because the slag is highly oxidizing in nature; it contains FeO; it contains MnO. So, these oxidizing slag if carried over during tapping into the ladle, then whatever amount of aluminum that is added into the ladle will react with the FeO and MnO of the carried over slag and it will form the inclusions. How it will form? For example, if I take reaction say 3 FeO plus 2 aluminum, that will give you Al 2 O 3 plus 3 iron; or for that metal, 3 MnO plus 2 aluminum; that is equal to Al 2 O 3 plus 3 Mn. In fact, the presence of Fe O is more important because Fe O is of the order of 16 to 20 percent. So, this reaction is more important.

If you see the stoichiometry of Fe O and aluminum reaction, what we say? That if 1 kg Fe O is carried over into a ladle, then it decreases aluminum. 1 kg Fe O decreases aluminum by 62 upon 216 kg; that is equal to 0.286 kg of aluminum. Now, this 0.286 kg of aluminum will form around 0.51 kg of Al 2 O 3. Now, the density of Al 2 O 3; let us take it around 4 gram per centimeter cube. If all the inclusions were spherical size of 1 millimeter diameter, then from volume, you can calculate around 240 inclusions will form just by carrying 1 kg of Fe O into the slag. So, my whole idea of calculating this is to emphasize the fact that during transfer of molten steel from converter or electric arc furnace or energy optimizing furnace to the ladle, the slag carry-over should be as minimum as possible. Therefore, what is important here – to adopt the method, which are called slag free tapping. Some of the methods I have already discussed in my BOF steel making lecture; in order to have slag free tapping, in the past so many years, so many methods are being developed and these methods are in use like slag cut ball method, stopper method, detection method and so on. So, these methods allow in fact slag free tapping and that is important.

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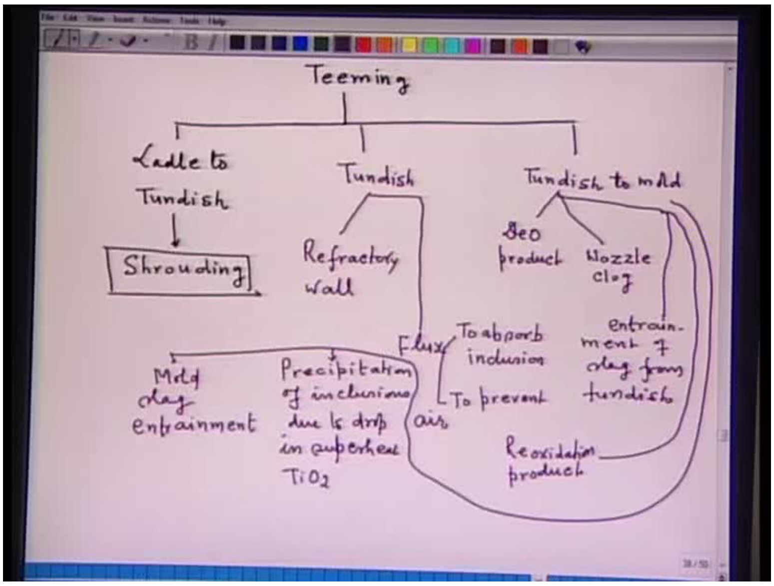

Now, another control where inclusion can be controlled is during teeming. There are… One is from ladle to another vessel for casting, which is called ladle to tundish. In this ladle to tundish, the stream is again… if it is bayer that is not covered by a refectory, then the oxidation will occur. So, here one has to provide the so-called shrouding of a stream. So, by shrouding the stream from ladle to tundish, one can control the inclusion formation. Then, molten steel is contained in the tundish because during the transfer from ladle to casting, for example, in continuous casting, tundish is the last refectory lined reactor, where molten steel is in contact with the refectory material. So, accordingly, the tundish can also contribute to large number of inclusions if proper control is not being done. What is the proper control? First, the steel is in contact with the wall; so, refectory wall is a source. That is, reaction between dissolved aluminum with oxygen of refectory lining; that is, when molten steel is poured into the tundish, it has free aluminum also. If the refectory is unstable, then aluminum can react with oxygen of the refectory lining and can form the so-called Al 2 O 3 inclusions. So, it says that the lining of the refectory of the tundish must be chemically stable, so that no reaction should occur.

Another important source, which can be controlled because the tundish or the molten steel in the tundish is covered by a flux. The fluxes are used to absorb inclusions; that means the fluxes should be also molten, so that any inclusion, which is rising from the bath of the tundish, should be able to be absorbed in the flux. Therefore, proper properties of the fluxes in the tundish are also important. Now, another important property that flux does; it shields the molten steel contained in the tundish from atmospheric reoxidation. So, it prevents to prevent air from atmosphere; that means the proper selection of the flux for tundish is important to control the inclusion formation.

Now, next point which can be controlled is from tundish to mould, because molten steel is poured from tundish to mould and there are several places where inclusion can occur. First, the deoxidation product, which are in the molten steel, can be directly transferred to the mould, because mould is used for solidification. Once steel is solidified, then whatever inclusion, which has been transferred from tundish to the mould, will remain entrapped into the solid steel. Another source is the nozzle clog because the molten steel is poured from tundish to the mould by submerged entry nozzles. If molten steel contains alumina inclusions, then alumina inclusions deposit on the walls of the submerged entry nozzle. Sometimes, these nozzle clogs can detach from the wall; they will again be carried over into the mould and will contribute to the formation of inclusions.

Now, third, where you can control is the entrainment of slag from tundish. How slag gets entrained? Yes, the casting proceeds, the molten steel level in the tundish falls during the ladle change over period. As a result of decreasing height of the tundish, vortex phenomena can occur. Because of the formation of the vortex phenomena, the slag which is present on top of molten steel in the tundish, may be drained and transferred to the mould; it may also cause inclusion. Therefore, to control the inclusion through vortex formation, it is important that a particular height of the liquid steel is maintained. That is particularly important during sequence casting, because during sequence casting, when the ladle is emptied and the next ladle, when it is arriving, the time, which is taken by arriving of the next ladle is important. If it is properly synchronized, then molten steel from the tundish will not fall to a height, where vortex can form. So, this is also an important thing.

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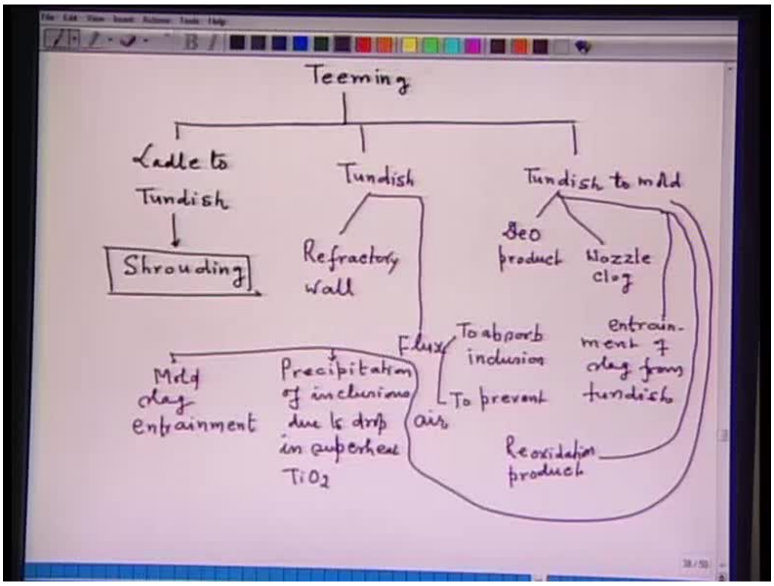

Other could be the air leakage in the submerged entry nozzle; that is, reoxidation product formed due to air leakage from whatever the source. Also, during continuous casting, mould is also covered by the slag. So, it is also possible mould slag entrainment, because sometimes the liquid steel in the mould is stirred for removal of the inclusions or for removal of the temperature gradient. So, in that process of stirring, the slag, which is on the top of the mould, may get entrained and may be picked up during solidification.

Then, the precipitation of inclusions due to drop in super heat; Now, all these things correspond to tundish to mould operation. Now, when the super heat drops or when the liquid steel cools, it solidifies; then, depending on the solubility limit, the elements in the steel can combine and an inclusion can precipitate, for example, Ti O 2; in titanium treated steel. Here the agitation of the bath in the ladle or in the tundish helps to float the inclusions. In fact, the ladle or tundish stirring is done to allow the inclusions to float.

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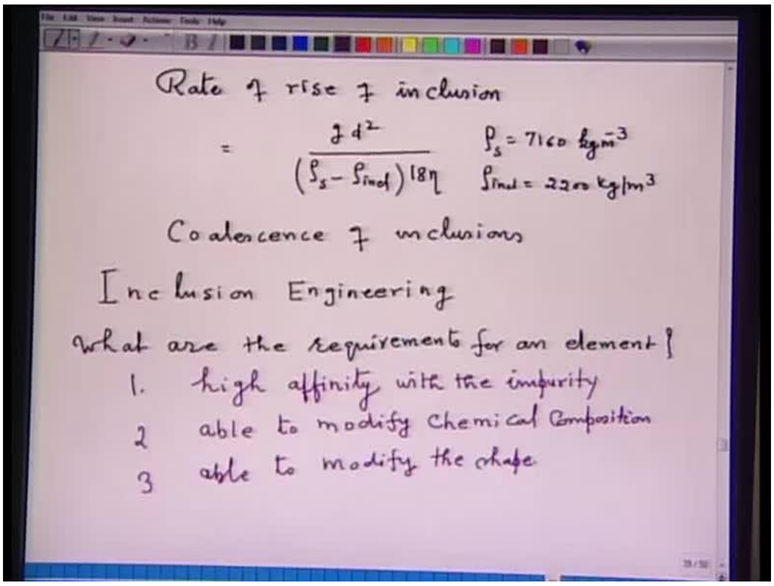

Rate of rise of inclusion

$$= \frac{g d^2}{(\rho_s - \rho_{incl}) 18\eta} \quad \rho_s = 7160 \text{ kg m}^{-3} \quad \rho_{incl} = 2200 \text{ kg/m}^3$$

Coalescence of inclusions

Inclusion Engineering

What are the requirements for an element?

1. high affinity with the impurity
2. able to modify Chemical Composition
3. able to modify the shape

Rate of rise of inclusion depends upon the diameter of the inclusion and the buoyancy force, that is, the density difference between the steel and the inclusion. As such, the rate of rise of inclusion is given by g d square upon rho s minus rho inclusion into 18 viscosity. Now, if I take rho s, that is, the density of steel as 7160 kilogram per meter cube and rho inclusion for example, 2200 kilogram per meter cube, then 5 micron meter and 50 micron meter spherical size nuclear inclusion will take 3000 minutes and 50 minutes, respectively to float a bath height of 2 meter. So, what is important from here is the coalescence of inclusion.

Smaller diameter inclusions will take a longer time to float; larger diameter of inclusions will take smaller time to float. Anyway, the problem is with the smaller size inclusion. If the inclusions can be coalesced or if they can be agglomerated by creating some sort of agitation condition, then they will become bigger in sizes and their floatation becomes easier. So, these are some of the ways in which the inclusion control can be done. All these ways are exercised, so that one can produce clean steel.

Now, enough we have said about the control of inclusions, about the removal of inclusions; we have come to a stage that it is not possible to produce steel without inclusions; that means, inclusion is a part of production of steel. If you want to remove them, a very long time is required in order the inclusions can float. Even then, it will not be possible to get rid of the inclusions, which are there in the molten steel. So, what should be done? That is where the important, is called inclusion engineering; it is what the inclusion engineering is important.

Now, in the inclusion engineering, what is done? An engineer does not bother about the inclusion, which are present, but what he does? He tries to modify the inclusion such that their harmful effects are minimized, because when it is true that we cannot produce steel without inclusion and to remove small size inclusion, we require a very long time, which may not be economically viable. Therefore, an engineering aspect of design of inclusion becomes very important. In fact, remember: inclusion engineering does not refer to removal of inclusions, but it refers to modify them in terms of chemical composition, so that their harmful effects can be alleviated. So, inclusion engineering also involves distribution of inclusion uniformly in the matrix, so that composite property of the steel can be utilized. What I wanted to say – in fact, inclusion engineering does not relate to removal of inclusions, but it relates to modify them. So, it is a practical way of modifying the harmful effects of inclusion into harmless effect or positive effect; if the inclusions can be distributed uniformly in the matrix, then in fact, you have produced a material, which is a composite material of very different properties.

In some cases, deliberate attempts are made to form verifying inclusions, for example, nitrides, carbonitrides inclusion in hardening steel. Now, such inclusions can form with oxygen, nitrogen, sulphur or carbon by adding elements which produce a very high melting point; for example, by adding titanium, tungsten and rare earth or aluminum, because they will produce a high melting point and that may be beneficial. In fact, that is what is meant under the term inclusion engineering.

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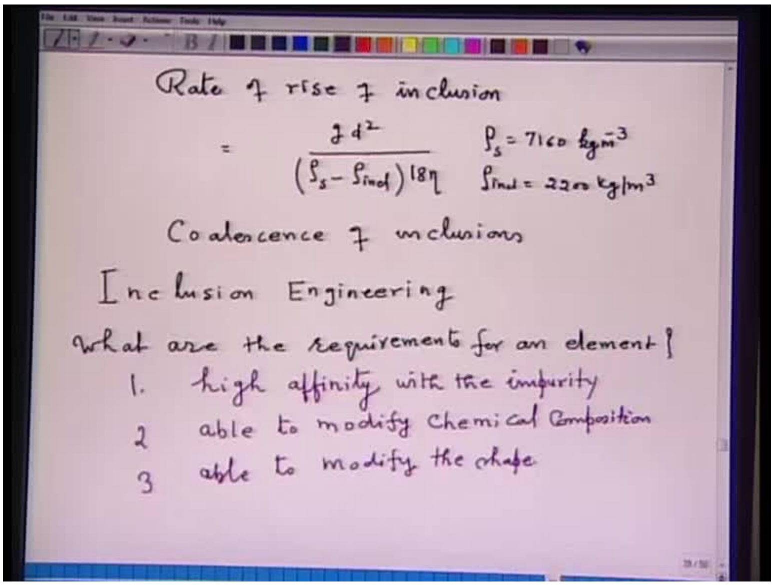

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Coalescence of inclusions

Inclusion Engineering

What are the requirements for an element?

1. high affinity with the impurity
2. able to modify chemical composition
3. able to modify the shape

Remember, the job of an engineer is to modify the inclusions, which are considered to be harmful, such that their harmful effects are converted either into harmless effect or positive effect; that is what an engineer does. How it can be done? If you just think, then it comes to my mind that one has to be in search of an element that can react preferentially with the impurity and do the job of modification. As such, what are the requirements for an element to be added?

What are the requirements? First requirement of this element should be - it should have high affinity with the impurity. In fact, it is the oxygen and sulphur; these are the two important impurities in the steel. We are looking for an element, which has a strong affinity with that impurity. However, if other impurities are there and if you want to modify, then we have to find an element, which has an affinity with that particular element. Second, we are looking for - that element should be able to modify chemical composition of an inclusion, so that if it is solid at the steel making temperature, it becomes liquid. If you could get that, it is a wonderful. Third is possible; it should be able to modify the shape – particularly, I am talking of the shapes like sharp corners, sharp edges, which are detrimental to the properties; those shapes can be converted to spherical.

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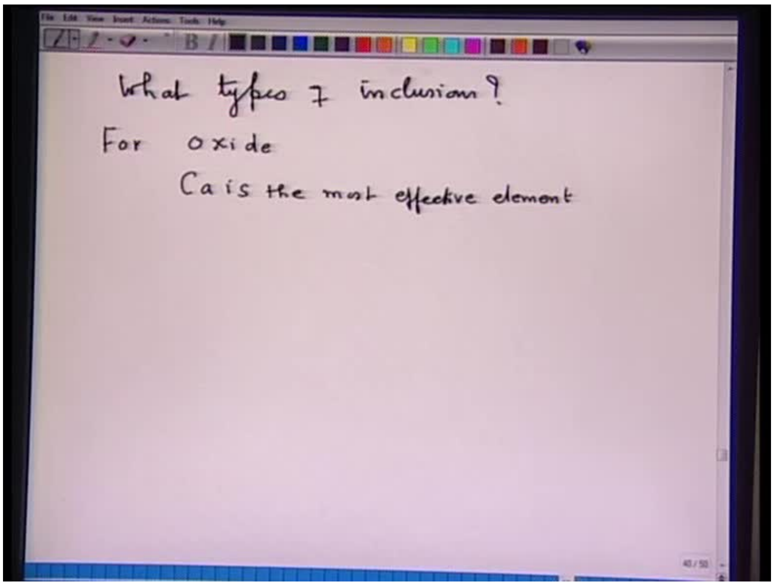

What types of inclusion?

For oxide

Ca is the most effective element

What types of inclusions that we are looking for modification? Now, for example, oxides and sulphides; oxide - for example, Al 2 O 3; Al 2 O 3 inclusions are very low deformable, and hence, they will break; that is not good. Similarly, manganese sulphide inclusions; if they are rolled, it will form a stringer type of inclusion. So, for oxide modification, calcium is the most effective element, because calcium has a very high affinity with oxygen. Mischmetal, which is an alloy of cerium and lanthanum, can also be used, but calcium is more powerful, and hence, calcium is used for modification of Al 2 O 3 inclusions.

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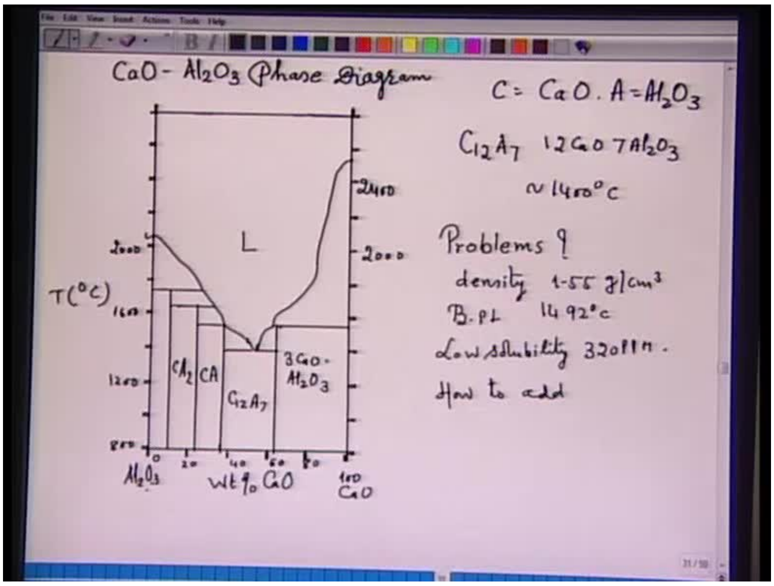

CaO - Al_2O_3 Phase Diagram

C = CaO. A = Al_2O_3

$C_{12}A_7$ $12CaO\ 7Al_2O_3$

~ 1400°C

Problems?

density 1.55 g/cm³

B.Pt 1492°c

Low solubility 320 ppm.

How to add

How it does? If you see this phase diagram of Ca O, Al 2 O 3, which I have sketched for you, on the x-axis, at this point is 100 percent Al 2 O 3 and this is 100 percent Ca O. So, if we add weight percent Ca O, then the melting point of the alloy, which forms Ca O, Al 2 O 3, decreases. In fact, if you see the composition corresponding to C12 and A7, that means, 12 Ca O and 7 Al 2 O 3, its melting point is around 1400 degree Celsius. Now, note: pure Al 2 O 3 has a melting point of somewhere around 2050 degree Celsius, which is solid at the steel making temperature; it is very difficult to remove. So, if we do a calcium treatment, then a composition is reached, where the melting point becomes minimum. This composition is 12 Ca O7 Al 2 O 3. However, there are also other compositions for example, Ca, which is Ca O Al 2 O 3; Ca2, Ca O2 Al 2 O 3 – all have melting point higher than 12 Ca O Al 2 O 3. So, it is attempted that by calcium injection, a compound formed, that is, 12 Ca O7 Al 2 O 3, which has a very low melting point is liquid and it can be made to float also. That is what the important point in case of modification of alumina by calcium.

Good, we have got an element. What are the problems? The problems in the calcium addition are as follows. Problems: calcium has a density, which is 1.55 gram per centimeter cube. What does it mean? It is very difficult to introduce into the melt, which has a density of 7 gram per centimeter cube. It has a boiling point 1492 degree Celsius. What does it mean? At the steel making temperature, which is 1600 is in the vapor form; vapor is highly reactive. Third, extremely low solubility in steel; solubility is of the order of 320 PPM. All advantages, which I have told you about the calcium addition, have gone now to development of a technology to make calcium available in the steel bath, because if you just do not think about that whatever calcium you add, it will float, it will all oxidize, it will not do your job. So, it boils down to development of a technology to inject calcium deep into the bath at least up to a depth where the effect of vapor pressure is minimized.

For that, the question comes the technology and question comes how to add. In the form of alloys, calcium silicide, calcium iron, calcium aluminum – these are the alloys type in which it is added in a wire form. There is a code wire in which calcium silicide is filled; these wires are available in the form of the roll. This calcium silicide powder is injected at a very high speed varying from 30 meter per minute to 300 meter per minute, so that it directly enters deep into the bath to counter the effect of vapor pressure, so that at that particular depth, calcium remains in the liquid form and it can do the job of inclusion modification rather than oxidizing itself. So, that is where the technological important.

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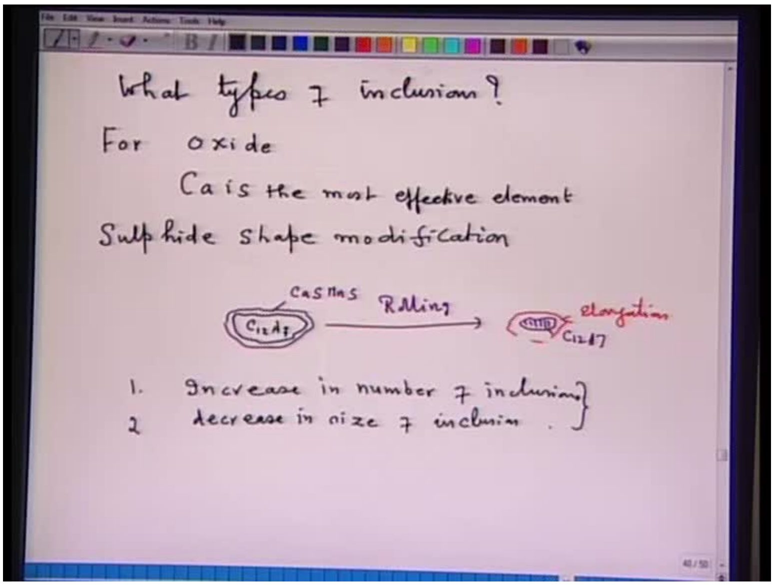

What types of inclusion?

For oxide

Ca is the most effective element

Sulphide shape modification

1. Increase in number of inclusion
2. decrease in size of inclusion.

Now, another issue is that of the sulphide shape modification. As you have seen, the effect of Fe S is counteracted by addition of manganese and they form manganese sulphide inclusions. Hence, you have alleviated the problem of hot shortness, but manganese sulphide inclusions on rolling forms a stringer type of inclusion. So, still you require a modification of this particular inclusion. So, we are looking for an element, which again has a strong affinity with sulphur; no doubt calcium has some affinity with the sulphur. However, when it is compared with the mischmetal, which is an alloy of lanthanum and cerium, the desulphurising ability of mischmetal is higher than the calcium.

Now, suppose if you do calcium, then calcium modifies the Al 2 O 3 inclusions and it forms 12 Ca O7 Al 2 O 3 inclusions. For example, if this is the inclusion, (Refer Slide Time: 44:54) which is (( )) C 12 A 7. Now, this 12 Ca O7 Al 2 O 3 inclusion has a very high sulphur capability. That means, it can absorb sulphur and on the top of this inclusion, one can have the so-called Ca S Mn S on the surface of the12 Ca O7 Al 2 O 3 inclusion; if you roll it, on rolling, it does not form a stringer type of inclusion. So, the center is again that of C 12 A 7; on rolling, this one is the elongation, which occurs. So, that way, the harmful effect of sulphide inclusions can be alleviated.

When mischmetal is added, the core of 12 Ca O7 Al 2 O 3 can be Ce 2 O3 or Al 2 O 3 based upon oxide; while, surface can be lanthanum sulphide and cerium sulphide. Now, for desulphrization, it is essential that oxygen content of the bath should be very low, because cerium and lanthanum will accordingly react with the oxygen and they form cerium oxide or lanthanum oxide. So, it is very essential that the bath should be deoxidized and then the mischmetal is to be added or calcium is to be added for sulphide shape modification. Now, addition of calcium or mischmetal has been done in one particular phase. For example, in duplex stainless steel, what they have observed that increase in number of inclusions; also, they have observed decrease in size of inclusion. As a result of both these effects, which they have got during inclusion modification by addition of mischmetal in duplex stainless steel, they could found that the hot ductility of a stainless steel has been considerably improved. Again, in another application, the addition of 0.2 to 0.3 percent of rare earth metal in steel for drill bit roller cutters, it reduces the oxide and sulphide inclusions in them to change their shape from sharp, angular and elongated to globular, and to decrease the grain size. As a result of these modifications of inclusions by adding cerium, the strength property and impact strength of cast metal increased. As a result of that, they could modify the inclusions by addition of cerium. Hence, the good property has been achieved.

What I have told you from here? These are the two examples, which I have said, but there could be many examples, where it is not required to remove all the inclusions. Simply just to modify, all that you have to find out an element. You can find out several such examples. So, in conclusion, what I want to say is that it is not always important to remove the inclusions. However, the bigger size inclusions are to be removed. However, the smaller size inclusions – it is not all the time required that you remove the inclusions. However, if those inclusions can be modified in terms of their melting point, or in terms of their sharp edges or corner edges modified to spherical globule, then it will be good. From application point of view, they will not have a harmful effect.