Hello and welcome to this manufacturing process technology part 2 module 19.

(Refer Slide Time: 00:17)

We were talking about electro chimerical machining.

(Refer Slide Time: 00:20)

Electrochemical Machining

And in context of that we had mentioned how this MRR of the material removal rate m dot could be represented by AI/ ZF where A the mass removal rate A is basically the gram atomic weight I is the current in amperes Z is 96500 and also told you how to arrive at this charge of 1 mole electrons and then Z is the balance E the particular ion that is electro chemical displaced and from using the density term in the expression we could actually calculate.

What is the value removal rate which is AI/ ρZ F cm^3/ s also we were talking or discussing about you know in real life we have really not single phases but alloyed systems where there are mix materials and then you know each of them would have a different density should them would have a different atomic weight and it becomes a little compression calculation wise to find out is the desolation density of electrode made out of an alloyed so I am going to now sort of talk about that aspect and give you a little more illustration into.

(Refer Slide Time: 01:25)

Anode made of Alloy

- When the anode is made up of an alloy instead of pure metal, the removal rate can be found out by considering the charge required to remove an unit volume of each element.

If the atomic weights and the valencies of corresponding ions entering the electrolyte are A_1, A_2, A_3....... and Z_1, Z_2, Z_3....... Respectively, and the composition by weight of the alloy is x1% of element 1, X2% of element 2........ then a volume v cm³ of the alloy would contain $v\rho x_i/100$ gram of the i th element, where ρ is the overall density of the alloy in gm/cm³. The charge required to remove the ith element in volume v is given by:

$(v \rho x_i / 100) . (Z_i F / A_i)$

The the volume of the alloy removed per unit charge is

$Q = (100/\rho F) (1/ \Sigma(x_i Z_i / A_i))$ cm³/ amp-sec or

$Q = [(0.1035 \times 10^{-4})/ \rho] (1/ \Sigma(x_i Z_i / A_i))$ cm³/ amp-sec

How an alloyed system can be worked out so when an node let us say is made of alloy and you know instead of pure metal the removal rate can be found by considering the charge required to remove an unit volume of each element okay and so if the atomic weights and the valances of the corresponding ions entering the electrolyte or let us there is a n atomic system or you know there are different n different pure phases which are there in the alloyed electrode so you have atomic weight A1 okay A2, A3 soon so forth as the different atomic weight soon up to n of the all participating pure phases.

And similarly the valances Z1, Z2, Z3 soon up to Zn and also if we assume that you know in the same using the same logic that the composition by weight of the different phase 1 to n in the alloyed system is X1 % of let us say A1, X2% A2 soon so forth up to XN% of the nth phase and we want to remove let us say a volume v cm³ of the alloy that would exactly conation let us say because you know the total weight obviously of the alloy would be the average density ρ average of the alloyed system this is the overall density of the alloy in gram / cm³ times of v which is the mass okay.

And so XI% of this mass in another words XI / 100 would be the amount of grams of the ith phase present in the particular alloy okay so the if we consider how many moles of the ith phases are present in this much amount of mass in grams of the ith so I just divide this v ρ average XI / 100 with respective AI which is the atomic weight of the ith phase so these many moles are

present okay that is how you find out you know from the grams to moles the how many moles are present.

And each mole because it is a ith phase and it is containing of LNC which is ZI would have exactly ZI charges to be transported so I would say if I just you know this is one mole you know present and then let us say if we have the electronic charge for 1 mole by just multiplying F with this which means that this much charge is present times of ZI because ZI is the valance supposing there is a calcium + 2 or a Fe +2 or F3+3 so you have 3 electrons to mobilize one atom in case of plus valency you have two electors to mobilize one atom in case of + 2 valances.

So on so forth so this is a ith violent state having zi balance valance so you should have exactly zi electrons, to mobilize the particular species the ith species in the electrode okay, so in other words the total amount of charge that is required to remove the ith volume i^{th} element in the volume V which we have remove from the alloy.

Is actually given by this term here V∂ average xi/ 100 times of zi f / ai okay, so that is how you give the total amount of charge required and obviously the volume of the alloy removed per unit charge would they actually be equal if I had you know the total amount of charge of all the I elements added together which I will actually in a more simplistically or more simplistic manner right here so we have let say I phases, I varying if doing 1 to m and we have from each phase contribution that is emerging.

Is V∂ xi / 100 times of zif / ai okay so this is a sort of σ indicating that over the n phases how much total charge, is needed okay to remove the volume V and so I can have the volume of the alloy per unit charge volume of alloy per unit charge as simply the volume V / this expression here, so I take out the V the ∂ average the 100 and also f okay and so we are left with here by varying 2 in 1 and 1 and n xi zi / ai okay.

So the V factor goes out and we are now left with and just simply 100/average density times of f times of σ I varying to in 1 to n xi zi / ai okay xi zi / ai then I can actually further just change everything here, by basically converting this 100/ f here you know into the corresponding value you know already the value of f = 96, 500 columns, and so this finally comes out be the, the volume per unit charge you know so this is volume of alloy removed per unit charge, so which is a very important.

Term from a context of material removal rate in case of alloyed systems, so let us now look into a little more you know numerical or ended approach not to predict some of these things.

(Refer Slide Time: 07:01)


For example if I would just give you a small situation where in a electro chemical machining process there is a pure iron work piece that is to be removed and we wanted to find out what is the volume removal rate, what is the current that is required for a certain volume removal rate which has been given here for example the volume removal rate here given as 5cm^3 per minute so the gram atomic weight, valency at which this dissolution will take place are resume to be 56 grams valency + 2 valance state and the density of iron is taken out to be 7.8grams /cm^3

So having said that if I just use the expression let us say the q. or the volume removal rate here which was cm^3/second is 5/60 cm^3/second obviously this minutes needs to be converted that is why this 6th term times or so this actually is equal to the atomic number A times or atomic weight A times of I the current total amount of current which flows into the circuit the electro chemical system.

Divided by the density which is 7.8 in this particular case times the valency times faraday constant 36, 500 so we can just simply plug in the values 56 times of I let us assume that we needed I amperes to do this kind of material removal divided by 7.8 times of two times of 96500 and so this makes I 2240 ampere so you can think of that you taking about 2 .24 kilo amps in order to remove a small volume as small as 5 cm^3/minutes.

And so this gives a very high level of specific energy for the this material removal rate or you know this kind of ECM or electro chemical machining process.
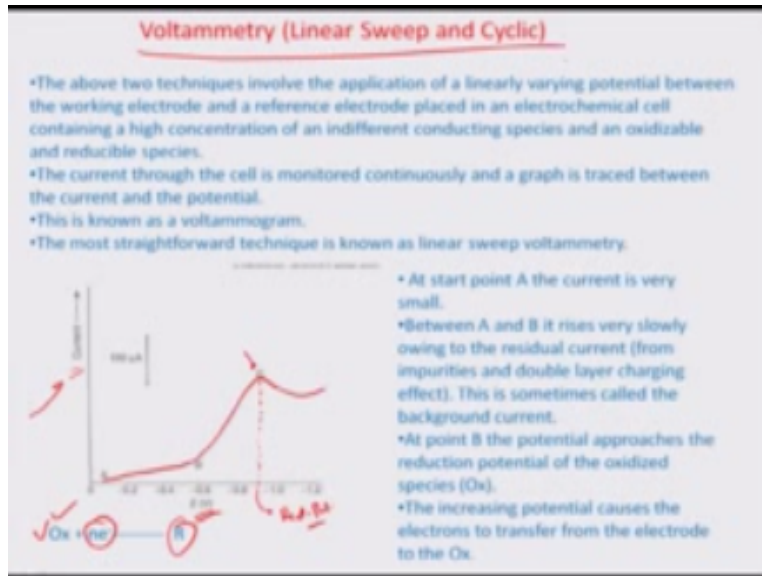
(Refer Slide Time: 09:28)
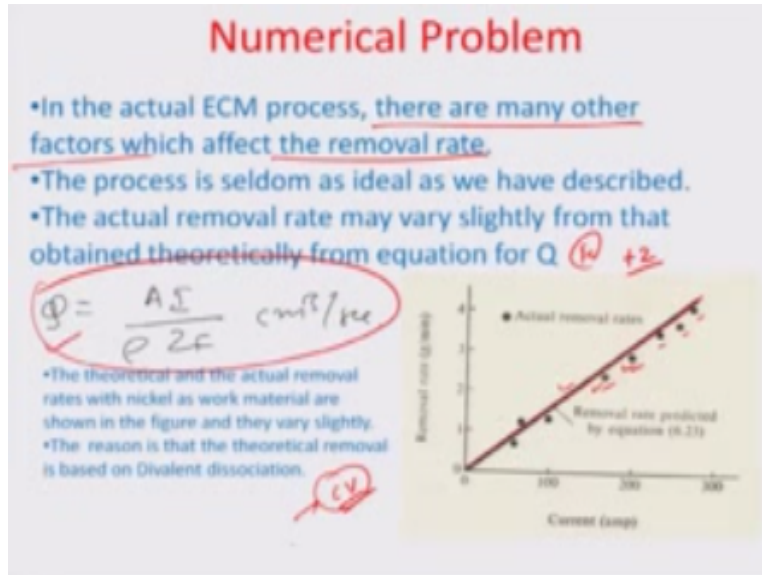
So in the actual you see however the many other factors which would affect the removal infact if I would look at this similar example you would see that the actual removal rates are slightly lower in comparison to the predicted removal rate which is given by this solid line right here and one of the reason is that we are not really consider the other valencies which are there and we have always consider the divalent solution in case of for example iron.

But what happens in actual situation is that there may be also a trivalent dissolution possible depending on how many valency states exist and so if that kind of a situation happens obviously then you cannot really predict whether an iron which is displaces a trivalent or a divalent and so actual removal rates are slightly lesser so they vary slightly from the theoretically obtained removal rate given by this expression right here, okay.

So we now actually try to do another aspect here which is also known as cyclic volumetric which is important for you to give feeling that what is this as a oxidation or reduction that we are actually trying to find out so you find out.

(Refer Slide Time: 10:42)

Voltammetry (Linear Sweep and Cyclic)

• The above two techniques involve the application of a linearly varying potential between the working electrode and a reference electrode placed in an electrochemical cell containing a high concentration of an indifferent conducting species and an oxidizable and reducible species.
• The current through the cell is monitored continuously and a graph is traced between the current and the potential.
• This is known as a voltammogram.
• The most straightforward technique is known as linear sweep voltammetry.

• At start point A the current is very small.
• Between A and B it rises very slowly owing to the residual current (from impurities and double layer charging effect). This is sometimes called the background current.
• At point B the potential approaches the reduction potential of the oxidized species (Ox).
• The increasing potential causes the electrons to transfer from the electrode to the Ox.

You basically if we look at this trend right here of a species which is actually getting reduce from an oxidized state and we see that there is a plot that I am revealing here which is between the current okay, current between the electrodes and the voltage that is being applied so you see that you know there is obviously a certain voltage which is corresponding to the reduction potential of this oxidants species here.

Where there is a certain release in the electrons and a sudden absorption of the electrons and there is suddenly a change in the current because of that, current obviously is a positive charge which is considered to be reverse of the electron one flow which happens in a circuit and that is how convention current is treated so obviously because of a sudden absorption of all the electrons together the current has increased.

You know because there is a again a whole movement and so you can think of it that if supposing there is a plot of current which is going on at a certain rate and then slightly change rate near about this point where it is corresponds to the reduction potential of these species there would be huge enhancement in the current and which should be represented by a peaks, so this is how mostly reduction potentials of or even the oxidation potentials at the matter actor found out in species. And this is this term is known as voltammetry so you can have either.

linear sweep or cyclic sweep meaning thereby in a linear sweep you only oxidize or reduce and in a cyclic sweep you do both of them together so you have backward voltage sweep and a

forward voltage sweep and you can increase the voltage per unit time between 2 volts, 4 volts, 5,6 volts something like that so you have 2 volts per minute let us say of 1 volt per minute.

So you keeping on increasing the voltage as a function of time and seeing at what potential exactly the reduction or the oxidation to the species are going to happen, that is how voltammetry is performed on most of these species and here we need to really find out that potential corresponding to which there is going to be a dissolution of the species because it is a micro machine or it is a electro chemical machining that we are talking about, so we need to at least understand this standard reduction potentials based on which we can actually put the location coordinates of ourselves in terms of voltage current relationship.

(Refer Slide Time: 12:58)

So when we talk about multivalent dissociation obviously is the current is more that the solution takes place at higher potential difference and there can be trivalent dissolution also occurring at a certain value of current and at larger current theoretical values tends to be more than the actual ones because obviously there are going to be many other states which are also going to participate in the process of dissolution.

Sometimes the dissolution valance also depends on the electro lights for example copper dissolves in mono-valent form of chlorine solution whereas a nitrate solution the dissolution

takes place in the divalent state. So this table here right here mentions some properties related to the different metals which participate in the oxidation reduction process the gram atomic weight the different valences of dissolutions that they may possess and the density that they have and this is important for calculations say particularly on a lot systems and we are going to now look at a problem an interesting problem of a multi phase alloy.

Called Numonic 75 that we want to find out for its removal rate in cm^3/m, we have given that a current of 1000 amperes is passed and we would now for now use the lowest valence of dissolution of each element although there is a possibility that based on where the oxidation or reduction potential lies of the cell, there may be a divalent or a trivalent state which comes in okay, so I am not going into that complexity right now we are just simplifying by saying that use the lowest valence state in this particular case, and so we are actually put into together this composition weight percentage of the Nimonic 75 alloy.

So let us the removal rate if we want to find out so the removal rate in cm3/ampere second or per unit charge has already been given by the earlier calculation that I showed you for Q is 0.1035 10^{-2} by the average density do average divided by σ, I varying between 1 and N in this case the there are at least 7 phases that we are talking about, so this N is actually 7 okay, xizi/Ai where

these i's are the ith phases properties including the percentage weight which is actually given here okay, so this is the weight percentage of the particular species i[th] species.

The valency which would be using is the lowest valency from the table earlier I have just given you this table you know right here and lowest valences are mostly you know in this case for example nickel would have +2, similarly chromium would have +2 again Fe is +2 so on and so forth. So only the lowest values are being used for the valencies z_i A_i obviously is the atomic number, so let us now find out the most critical term here which I would like to first get into the average density, okay so first let us find out the average density ρ average of the alloy.

(Refer Slide Time: 16:23)

So ρ basically ρ average can be given as 100/I wearing between 1 to 7 okay x_i/ ρ_i, so I am considering here overall base weight of 100grm and in 100grms as I have earlier illustrated there are 7 species each of them having gram weights like this is 72.5 gram, and 19.5grams, 5gram, 0.4 gram, 1grm, 1grm and o.6 gram respectively. So what we are trying to do is to see that each of the phase has how much contribution in terms of volumes, so 72.5 gram nickel for example would have exactly volume equal to 72.5 grams by the density of the nickel okay.

So we just do the summation of that total volume of each phase, so that mass per ended volume can be calculated on the average basis. So you have 100grams/ that is now put the values of the different species here we have 72.5 grams of nickel / it is atomic divided by its density mass density which is 8.9 gram per cm^3, we just borrowing it from this table okay, so there is a density

column here for nickel we have 8.9gram per cm^3 so we do it for remaining phases as well not going to again and again refer back to the table but just giving you the values here 19.5/7.19+ 5.0 / 7.86 + again 0.4 / 4.51 + again 1.0 / 2.33+ 1.0/ 7.43 + 0.6 / 8.96.

So the total average density happens to be equal to 8.15 + 2.171 times inverse of this in to 100 whatever I am saying, so + 0.09 + 0.43+ 0.13+ 0.07 okay, so this becomes equal to 8.18 gram per cm^3 so the average density of this particular alloy comes out to be 8.18 grams percm^3.

(Refer Slide Time: 19:10)

Let us take this back to the equation that we had earlier relationship that we had earlier seen between the value q that is the volume per unit charge and the average density, so this is 0.1035 10-2 / the average density which is 8.18 bar the previous time of one / this whole expression here so we have 72.5 times of the valiancy the lowest valiancy is that / the atomic weight of nickel plus similar exercise for the other phases are present 19.5 x 2 / 51.99 + 5 x 2 / 55.88 + 0.4 x 3 / 47.9 + 1x 4 / 28.09 + 1x 2 / 54.94 + 0.6 x 1/ 63.57.

So this in totality results in 0.1035 10^{-2}/8.18 times of 3.6 in other words 0.35 10^{-4} in the units here is centimeter cube per ampere second meaning volume per unit charge which is being removed now you have already know that thousand ampere or one kilo ampere current is used the removal rate therefore would be equal to 0.35 10^{-4} times of one thousand okay.

The times of if I wanted to find this in centimeter cube per minute just multiplying this 60 is 2.1 cm^3 per minute okay so that is how you can find out the volume removal rate Q. okay of the alloyed systems given the various components for the different weights and the different atomic rates and other properties associated with this whole set up let us now go into a little different problem about realizing what are the impacts of the different potential zones which are formulated from this solution to the solid electrode or vice versa on both sides.

(Refer Slide Time: 21:49)
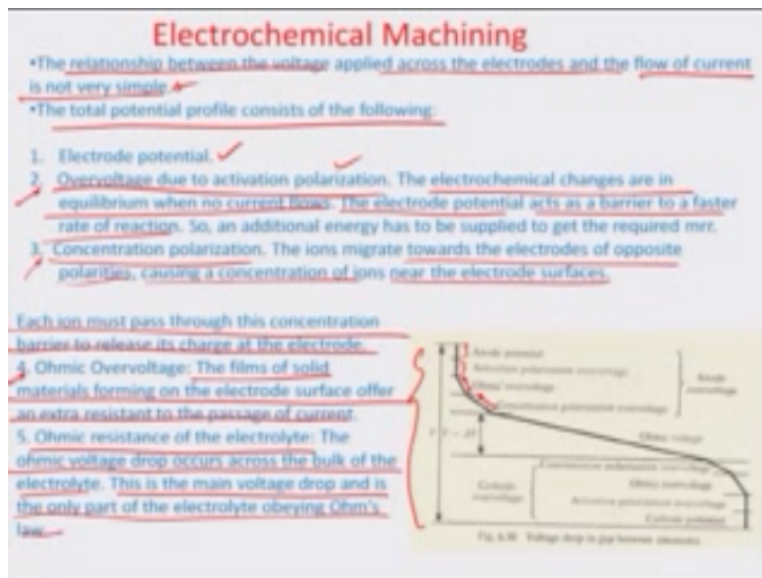
So in electrochemical micro machining when we are machining when we are talking about the relationship between voltage applied across the electrodes the few of current has we all realizes not very simple it is because the charge transport has to take place crossing the diffuse layer and the double layer and then finally an interaction in terms of you know the transport in to the electrode from the electrolyte and vice versa.

So the total potential profile would consist of the following one is obviously the electrode potential the other is the over voltage due to activation polarization the electro chemical changes are in equilibrium when no current flows so the electrode potential axis are barrier to a faster rate of reaction when additional energy obviously has to be supplied to get the required MRR just because of this polarization.

And there is dual layer that has to be crossed by the ions so that you know that particular potential has to applied from outside okay so it is sort of work done on the ion to the cross over

this dual layer then we have something called concentration polarization obviously the ions migrate towards the electrodes of opposite polarities and causes of concentration a super concentration of the ions near the electrodes.

So I think I had given a very clear illustration when we are discussing about this dual layer that the concentration polarization you know if you look at the refuge of the ion go slower and slower as it goes near the electrodes and that is because there is going to be a accumulation of the ions of the opposite kind just near the electrodes and creates some kind of barrier for the other ions to get migrate.

So that is another polarization so you have a over voltage due to activation polarization when at the initial at then obviously as the ions are migrating towards the electrodes also there is some kind of concentration polarization each mine has to passed through this concentration barrier to release it charge at the electrode which is not easy.

And then obviously there is an omic over voltage which is because films of solid materials may form on the electrode surface which offers an extra resistance to the passage of the current and then finally there is an omic resistance of the solution itself from all this different barriers being crossed over.

And then you change a potential from the anodes and cathodes okay so there is some kind of a omic resistance of the electrolyte which it offers and follows simple laws but obviously the resistivity to high or the conductivity too low from the solid to the solution okay so the omic voltage drops occurs across the bulk of the electrolyte this is the main voltage drop and it is only part of the electrolyte through this law.

So if we avoid to plot all this on a voltage scale between cathodes surface and anode surface as been illustrated here there would be some part of it which is the potential some other part which is the activation polarization there is of course a thin film resistance which happens because some deposition of it would take place and add electrodes called the omic over voltage and then obviously there is a concentration because once the ion transports starts happening there is a diffusion gradient created by concentration dx and both the electrodes and then finally there is atomic voltage drop you know from one of electrodes to other that comes in. so this results in

over voltage and cathode over voltage barrier which needs to be necessarily crossed to getting into the omic zone for the electrolyte.

So therefore there is always an over voltage potential that as to be given which is also known as v- Δv, this Δv has to be given a excess for MRR to happen because these potential barriers are always hindrance to the ion transfer process. So while doing electro chemical machining you has to always obey, the fundamental rule that there has to be not only the red ox potential at which the dissolution will start to happen because of the oxidation reaction, the reduction reaction taking place simultaneously.

But also you have to consider in order reaching that potential point you have cross several barrier layers and therefore slightly extra voltage needs to be provided, for such barriers to be crossed over, so that you are exactly at that point where oxidation reduction happen within the electro chemical machining apparatus, so obviously the total over voltage of an anode.

(Refer Slide Time: 26:35)

If that is consider to be ΔV and the applied voltage is v, the current then is given actual current is given by V - ΔV/R, so this determines what is actual MMR, you have to always make these

substitution. Other word is ΔV if you can provide and be sure and then you can get the MMR that you need at a particular current. So R is the ohmic resistance of electrolyte. Now the conductivity is the tool and the work piece are much larger because they are metals okay and the conductivity of the electrolyte is not so large.

Typically the electrolyte conductivity may be around 0.1 to 1.0 where as if you look at something like iron which can be easily anode where the machine can take places about 10^5, so huge it is about 1,00,000 times more in comparison to the conductivity of the electrolyte as such. The surfaces of tool and work piece can almost be consider to be potential, we are not really concern with the potential effects that would happen because of dis parties on the surface in terms of roughness, asperities or valleys you know.

So therefore we really do not consider it to be as far as the potential calculation at a macro level goes, consider it to be atomically flat but actually that is an assumption because in reality when we talk about micro machinating process and this goes to the lower scale. We have to consider even those asperities and the potential constitution effect that it would produce and assume on this surface which will result into a lot of differences, in terms of machining is going to take place.

The conductivity of the electrolyte obviously is not really constant because of temperature variation accumulation of pebbles also aspartic dissolution of the anode, which results in some small areas which would be islands and I am going to talk about this great details when we talk about effects in CM and obviously when we go to the micro level and do cm micro machining these factors have to consider and in great details at that time.

So I would like to end up this volume in the interest of time, but in the next module we are going to little bit more about the understanding of how the two electrodes would be behave with respect to each other. We can call this topic the kinetics and dynamics of ECM process. So as if now I would like end this module thank you very much.

NPTEL Team
Sanjay Pal
Ashish Singh
Badal Pradhan
Tapobrata Das
Ram Chandra
Dilip Tripathi
Manoj Shrivastava
Padam Shukla
Sanjay Mishra
Shubham Rawat
Shikha Gupta
K.K Mishra
Aradhana Singh
Sweta
Ashutosh Gairola
Dilip Katiyar
Sharwan
Hari Ram
Bhadra Rao
Puneet Kumar Bajpai
Lalty Dutta
Ajay Kanaujia
Shivendra Kumar Tiwari

an IIT Kanpur Production