

Microsystem Fabrication with Advanced Manufacturing Techniques
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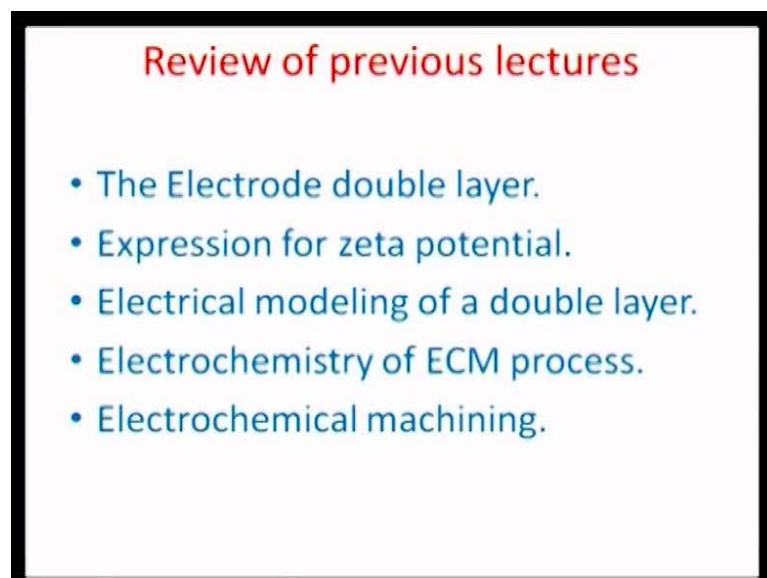
Lecture – 13

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Hello and welcome back to this lecture 13 on Microsystems Fabrication by advanced Manufacturing processes.

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So, brief recap of what we did last time, we studied about electrode double layer theory. The expression for the zeta potential we tried to derive with respect to an electrode, where zeta potential is the potential which is generated by any surface which comes in contact solid surface coming in contact with solution. And then we of course, modeled electrically the double layer try to understand, how potential varies with respect to distance x in the single direction from the electrode, and then of course we started understanding some of the basic electrochemistry behind the electrochemical machining process ECM process and as such started deriving things like material removal rate etcetera by faraday's laws of electrolysis.

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Electrochemical Machining

- The gram equivalent weight of the metal is given by $\epsilon = A/Z$, where A is the atomic weight and Z is the valency of the ions produced.
- The rate of mass removal is given by: $m \propto \frac{A}{Z} \cdot \frac{I \cdot t}{F}$
- If density of the anode material is ρ , the volumetric removal rate is given by: $Q = \frac{A}{\rho Z F} \cdot I \cdot t$
- Where:
 - A = gram atomic weight of the metallic ions,
 - I = current (amperes)
 - ρ = Density of the anode (gm/cm^3)
 - Z = valency of the cation,
 - $F = 96,500$ coulomb

Handwritten notes:

- $m = A/ZF$
- $\rho \cdot \dot{m} = \frac{A}{Z} \cdot \frac{I}{F}$
- $\dot{m} = \frac{A}{Z} \cdot \frac{I}{F}$
- $Q = \frac{A}{\rho Z F} \cdot I \cdot t$
- $\epsilon = \frac{A}{Z}$ (1 mole of a species whose weight is A of Z valent)
- $\epsilon = \frac{A}{Z}$ (no. of moles of charges)
- $\frac{I}{F} = \frac{60230 \times 10^{23} \times 1.6 \times 10^{19}}{96500} \approx 10^5$

So, today we have just an extension of that. So, what we started doing is basically understanding how mass flow rate in terms of deposition or dissolution on electrochemical process would happen and it is given by the Faraday's law. Where the Faraday's law says that the total amount of mass removed is proportional to the current. That is passed through the solution, the time for which it is passed and something called epsilon, where epsilon is this electrochemical or the atomic weight equivalent or equivalent atomic weight of particular species, which means, in term that 1 mole of a species whose weight is the atomic weight A of a valency z ? So, of z valent states would have an equivalent weight epsilon of A by z ; that means, is something like the amount of charge which would be needed to remove so much amount of weight. So, its gives an indication of that. So, basically that is what the atomic the equivalent atomic weight

epsilon is and of course, current time product is basically the amount of charge which is send into the system. The electrochemical system, which does either dissolution or deposition in as an electrochemical process. So, here we can always say that the mass removal rate that is \dot{m} , as can be illustrated in this formula here, is actually equal to the amount of equivalent weight that a person or that the material would have that is A by Z times of, an idea of what is the how many number of moles of current which is charge per unit time dq by dt is flown into the system.

So, the charge per unit time which is flown into the system in terms of number of moles of charges so moles of charge per unit time. So, this is given by the term I by F , where f as I already mentioned is this 96500 coulomb, which is actually the charge of 1 mole electrons 6.023×10^{23} times of 1.6×10^{-19} this is the charge on 1 electron. So, 1 mole electrons would have total charge of 96500 coulombs. So, that is what the faraday f term would be in this process.

So, I by F is really indicative of the number of moles of charges per unit time, which flows into the system. So, an if... So, many moles of charges are really needed A by Z charges are needed for this amount of grams which is coming out. So, A Z by A by Z times of I by F would actually give the amount of mass rate of removal, the amount of mass which is coming out. So, in terms of if you include the density factor ρ of the anode in grams per centimeter cube, the mass flow rate and density equated together would result in the volume flow rate.

So, Q is actually \dot{m} by ρ which is equal to A I by ρ Z F and this is in centimeter cube per second this is the volume rate of removal of a material of an electrochemical process. So, this is very standard formulation of how Faraday's laws can be utilized in actually, trying to find out what is the material rate of removal of some particular electrode. Which is deposited or which is actually stationed in some solution. So, this is true.

So, far single space system where there are not multiple components or multiple metals, which are involved in the electrode which is of a single metal or a single material or the removal that you are doing on single material; however, in engineering situations real life problems really you will actually not working on direct metals, but on alloys because alloying actually improves the system properties and engineering materials are really

alloyed compositions most of the time. And so therefore, this extension of this electrochemical basis of material removal has to be in an alloyed system as all where there is not a single phase as a 1 metal, but variety of phases in mixture with each other.

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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, \dots and Z_1, Z_2, Z_3, \dots respectively, and the composition by weight of the alloy is $x_1\%$ of element 1, $x_2\%$ of element 2, ..., then a volume $v \text{ cm}^3$ 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/cm^3 . The charge required to remove the i th element in volume v is given by:

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

The the volume of the alloy removed per unit charge is

$$Q = (100 / \rho F) \left(1 / \sum (x_i Z_i / A_i) \right) \text{ cm}^3 / \text{amp-sec or}$$

$$Q = [(0.1035 \times 10^{-2}) / \rho] \left(1 / \sum (x_i Z_i / A_i) \right) \text{ cm}^3 / \text{amp-sec}$$

$V \text{ cm}^3$ = volume of the material to be removed

ρ = average density of the alloy

Contribution in the mass of alloy is noted

$(V \rho x_i / 100)$

A_1	Z_1	x_1
A_2	Z_2	x_2
A_3	Z_3	x_3
A_i	Z_i	x_i

So, we will have different atomic weights of these phases we will have different densities of these phases which are in dissolution, and therefore a complex system emerges because of the application of this straight forward single metal case into that alloyed system. So, let us look at a problem example of that sort as mentioned here. So, let us say the anode now is made up of an alloy instead of a pure metal and the removal rate can be found by considering charge required to remove an unit volume of each element.

So, if the atomic weights and valencies of the corresponding ions entering the electrolyte are A_1, A_2, A_3 so on and Z_1, Z_2, Z_3 so on respectively. The composition by weight of the alloy let say is x_1 percent of the element 1 which has an atomic weight of A_1 and valency in which it comes out as Z_1 . So, this is the valency state which actually comes into question when this material gets removed from the particular electrode. The atomic weight A_2 and its valency Z_2 , the atomic weight A_3 its valency Z_3 so on so forth respectively. And the composition by weight of this alloy is may be let us say x_1 percent of A_1 , x_2 percent of A_2 , x_3 percent of A_3 so on so forth.

The whole idea is about the removal of a volume v centimeter cube of this alloy, where all this paradigms need to be somehow integrated. So, that total amount of volume that is

removed is v centimeter cube. And how much will that contain in terms of the mass. So, if v centimeter cube is the total volume of the material that is to be removed. So, the amount of mass that it would contain would actually be $v \rho$. Where ρ is the average density and this is something we need to find out in the practical application. I will just little know once we do a numerical problem. So, average density of the alloyed system.

So, $v \rho$ is basically the total amount of mass which is contained in v centimeter cube volume. And out of which, as I have already told the system has different species of atomic weights $A_1 A_2 A_3$ of different valencies $Z_1 Z_2 Z_3$. So, on up to you know, some n may be component and then in different percentages $X_1 X_2 X_3$ so on so forth. So, therefore, it is the total amount of contribution, in the mass $v \rho$ coming out of the i 'th metal. Let us so on so forth you have a case where you have the i 'th metal of percentage x_i with the valency z_i in weight equivalent... I mean atomic weight of a_i .

So, if the i 'th metals this formulation. So, called would get converted into $v \rho x_i$ by 100. So, this much is the mass contribution of the i 'th metal in the total mass $v \rho$ of the alloyed system. Where we assume that v volume centimeter cube are v centimeter cube volume is coming out of the system. So, this is the mass in grams of the i th element and we need to somehow develop a strategy to calculate this overall average density of the whole alloyed system. And this will come in practical application, where you compare the densities of the different components of a system and try to somehow average it looking at the different percentage contributions that those independent elements corresponding to i equal to some value would have in the overall system.

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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 a 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, \dots and Z_1, Z_2, Z_3, \dots respectively, and the composition by weight of the alloy is $x_1\%$ of element 1, $x_2\%$ of element 2, ..., then a volume $v \text{ cm}^3$ 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/cm^3 . The charge required to remove the i th element in volume v is given by:

$(v \rho x_i / 100) \cdot (Z_i F / A_i)$ *check unit*

The volume of the alloy removed per unit charge is

$Q = (100 / \rho F) \cdot (1 / \sum (x_i Z_i / A_i)) \text{ cm}^3 / \text{amp-sec}$

$Q = [(0.1035 \times 10^{-2}) / \rho] \cdot (1 / \sum (x_i Z_i / A_i)) \text{ cm}^3 / \text{amp-sec}$

Handwritten notes:

- V_{cm^3} = volume of the material to be removed
- ρ = average density of the alloy system
- Contribution in the mass of the alloy system
- $\frac{V_{cm^3}}{100} \left(\frac{Z_i F}{A_i} \right)$ = mass of the system

Diagram: A table showing the contribution of each element to the total charge:

Element	Weight %	Atomic Weight (A_i)	Valency (Z_i)
1	x_1	A_1	Z_1
2	x_2	A_2	Z_2
3	x_3	A_3	Z_3
...

Total charge = $\sum \frac{V_{cm^3} \cdot x_i \cdot Z_i \cdot F}{100 \cdot A_i}$

So, the amount of charge that is required to move the i 'th element in the volume v is given by the formulation. This mass removal times of $Z_i F$ by A_i . And that is so because of the fact that, if this were the mass of the i 'th system. So, the amount of moles which are there in this mass, assuming A_i to be the atomic weight of this particular system would be given by $v \rho x_i$ by 100 times of A_i . And so many moles need to be removed meaning thereby, that these are at Z_i valency state, meaning thereby the amount of charge that would be needed to be removed is so many moles times of the valency state. So, so many electrons or so many moles of electrons would be needed to remove this charge.

So, the amount of charge that is required to remove this metal material would be, $v \rho x_i$ by 100 A_i times of, the total charge in 1 mole electrons that is 96500 coulombs. So, that is the overall charge which is needed to remove the i 'th element in the volume v of the given alloy composition. So; obviously, if this is the charge per unit volume, the volume per unit charge would simply be a reciprocal of this and therefore, the volume per unit charge of the alloy removed per unit charge is given by this formulation right here. Which is simply a reciprocal of this term here, so amount of volume of the alloy removed per unit charge is simply given by the formulation just the inverse of whatever is mentioned here and that is basically can be represented as 1 by $v \rho x_i$ divided by 100 times of $Z_i F$ by A_i .

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Numerical Problems

In an electrochemical machining process with a pure iron work-piece, a removal rate of $5 \text{ cm}^3/\text{min}$. is desired. Determine the current required.

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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 a 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, \dots and Z_1, Z_2, Z_3, \dots respectively, and the composition by weight of the alloy is $x_1\%$ of element 1, $x_2\%$ of element 2, ..., then a volume $v \text{ cm}^3$ 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/cm^3 . The charge required to remove the i th element in volume v is given by:

$(100/pF) \cdot (1/Z_i A_i)$ *Charge / vol*

The volume of the alloy removed per unit charge is

$Q = (100/pF) \cdot (1/\sum (x_i Z_i / A_i)) \text{ cm}^3/\text{amp-sec}$

$Q = [(10 \cdot 1035 \times 10^2)/p] \cdot (1/\sum (x_i Z_i / A_i)) \text{ cm}^3/\text{amp-sec}$

Handwritten notes:

- $V \text{ cm}^3$ = volume of the material to be removed
- ρ_{avg} = average density of the alloy
- Contribution in the mass of alloy is noted
- $\frac{V \rho x_i}{100}$ = mass of A_i
- Mass of A_i

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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 a 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, \dots and Z_1, Z_2, Z_3, \dots respectively, and the composition by weight of the alloy is $x_1\%$ of element 1, $x_2\%$ of element 2, ..., then a volume $v \text{ cm}^3$ 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/cm^3 . The charge required to remove the i th element in volume v is given by:

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

The volume of the alloy removed per unit charge is

$$Q = (100 / \rho F) \left(\sum x_i Z_i / A_i \right) \text{ cm}^3 / \text{amp-sec}$$

$$Q = ((0.1035 \times 10^{-2}) / \rho) \left(\sum x_i Z_i / A_i \right) \text{ cm}^3 / \text{amp-sec}$$

$$= \frac{1}{\frac{\rho F}{100} \sum \frac{x_i Z_i}{A_i}}$$

Total removal = $V \text{ cm}^3$

$$V = \frac{100}{\rho F \left(\sum \frac{x_i Z_i}{A_i} \right)}$$

So, therefore, the volume of the alloy removed per unit charge is basically the reciprocal of this. As I mentioned before mentioned earlier, is just simply the reciprocal of this particular term as you can see here. So, let us just look at what the reciprocal would be like. So, we have 1 divided by $V \rho x_i$ by 100 times of $z_i F$ by A_i , A_i is this i is the subscript. So, of the i 'th element in the alloyed system. So, this can be further written down as 100 by ρF these really are constant this is the average density of the alloyed system. This F is having a value 1 mole charge of 1 mole electrons which is 96500 coulombs.

So, you can consider these outside the whole you know variable terms or outside the scope of the variable terms. And the other part basically is 1 divided by volume times of $z_i x_i$ divided by A_i . And for V volume, because total removal is V centimeter cube, the amount of charge that would be needed is really V for a unit volume this is the charge which is needed. The total volume V centimeter cube would be V divided by this value here. V divided by $V \rho x_i$ by 100 times of $z_i F$ A_i . So, this really goes to a situation where this v is eliminated because it is per unit V volume. And the total amount of charge so needed per unit volume is 1 by or 100 by ρF times of $\sum x_i z_i$ time divided by A_i .

Why \sum because, as you know that there are i components and this i varies between 1 and n . So, really looking at individualistic components where i can be 1 to n the total. So, called volume of alloy removed per unit charge, can be represented as this whole term 100 by ρF 1 by $\sum x_i z_i$ by A_i . There are certain connotations you can use here for

example, if you put the value of f here as 96500 the 100 by F term comes out to be about 0.1035×10 to the power minus 2 . So, ρ value and then this whole 1 by $\sum \xi_i z_i$ by A_i is the total amount of volume of the alloy removed per unit charge, volume unit is centimeter cube and charge is ampere second. And that is how, that is the amounts of you know this very critical for the whole electrochemical operation of an alloy. So, let us look a practical alloying system and try to see how to calculate this ρ average of the alloy. And how to calculate overall the volume of the alloy removed per unit charge that is given.

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Numerical Problems

In an electrochemical machining process with a pure iron work-piece, a removal rate of $5 \text{ cm}^3/\text{min}$ is desired. Determine the current required.

The gram atomic weight, valency state of dissolution, and the density for iron, 56 gms , $+2$, 7.8 gm/cm^3

$$m = \frac{A \cdot I}{Z \cdot F} \quad \text{or} \quad Q = \frac{A \cdot I}{Z \cdot F} \quad \frac{\text{cm}^3/\text{sec}}{\text{cm}^3/\text{cm}^3}$$

$$\frac{5}{60} \text{ cm}^3/\text{sec} = \frac{56 \times I}{7.8 \times 2 \times 96,500}$$

$$I = 224 \text{ amps}$$

So, to begin with let us look at an electrochemical machining process with pure iron work piece, where a removal rate of 5 centimeter cube per minute is desired. And we will have to determine how much current would be needed in AECM process for that. So, let say if you look at, the gram atomic weights table. So, the gram atomic weight and of course, the valency state of dissolution, and also the density comes from the standard table as for particularly for iron, because iron is the material to be removed comes out to be equal to 56 grams mostly iron goes in a divalent state.

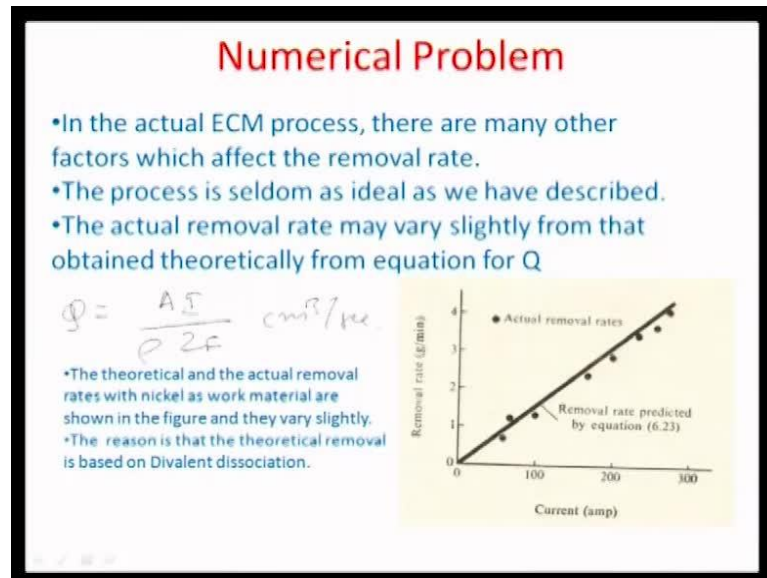
So, z equal to plus 2 and then the density of iron happens to be about 7 point 8 gram per 70 per centimeter cube. We already know that, m dot or the material removal rate is given by an expression A_i by ZF , this is the pure alloy this is the pure system. There is no alloying component as such in this m dot is also expressed in terms of volume rate of

removal Q as AI by ρZF this is in centimeter cube per second. And we have our volume removal rate which is intended in per minutes. So, we have 5 by 60 centimeter cube per second should be equal to atomic weight of iron, which is 56 grams times of the current desired. Which we need to find out divided by the density 7.8 grams per centimeter cube times of the valency state.

So, it comes as a divalent dissolution and of course, the faraday value which is 96500 coulomb. And other words calculating this for I you get varies, I value of about 222240 amps. So, what I want to bring to your notice is that a very small removal rate of only 5 centimeter cube per minute, which is actually very small in terms of conventional machining processes that, the machining would happen. In this electrochemical machining a such a high current value is needed, about 2300 amperes has needed 2.3 kilo amps. So, again it proves out that whether it is a mechanical process or whether it is in chemical process or electrochemical process.

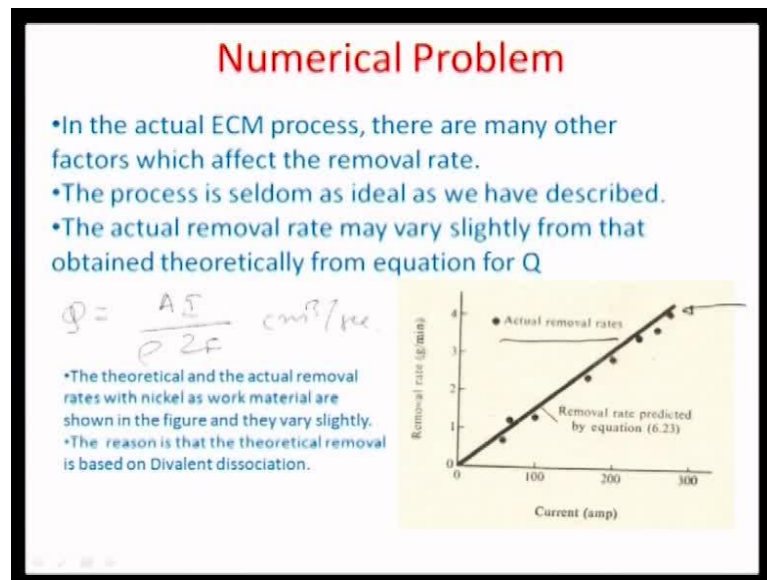
In general, this advanced manufacturing methods do have a very high energy requirement, but of course, there are connotations like, you know being able to produce complex shapes or being able to produce the desired roughness's which allows us to use these methods over some of the conventional strategies, which are widely available. So, that is the utility of be it electrochemical machining, be it abrasive jet machining, be it ultrasonic machining or any other nonconventional. So, called advanced manufacturing domain.

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So, the main key is the complexity which you have to take into account for design for manufacturing it. And the main key also sometimes is the surface roughness or the surface finish of a particular part. And that is why, nonconventional and advanced and the that is why the utility of such machining fabrication regimes for Microsystems engineering and Microsystems design and fabrication. So, let us look at another alloyed system as I just told. So, and just before you know looking at an alloyed system there are certain other very fundamental level things which need to be taken care off. So, the first thing, that I would like to tell here, is that in an actual ECM process, there you know, the many other factors also which remove or which influence the material removal rate.

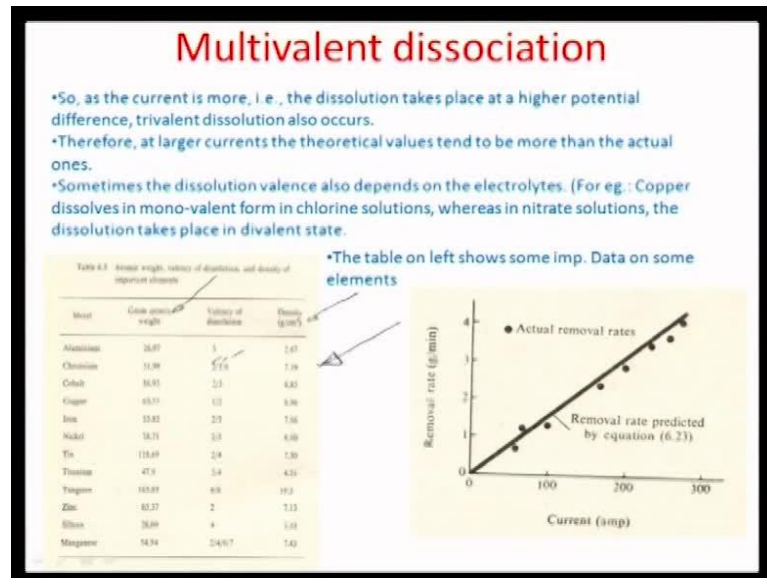
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If you look at really a simile between the actual removal rate given by this dots here. And the theoretically predicted rates given by this straight-line there is some variation some level of variation. And 1 of the main reasons is that, the sometimes you know the theoretical removal rates are only based on 1 prominently available valency states of the material, but actually it may happen that the material may come out in more than 1 valency states. For example: iron can exist as a ferric state plus 3 or ferrous plus 2 in case copper may exist is a plus 2 cuprous or plus 3 cupric state.

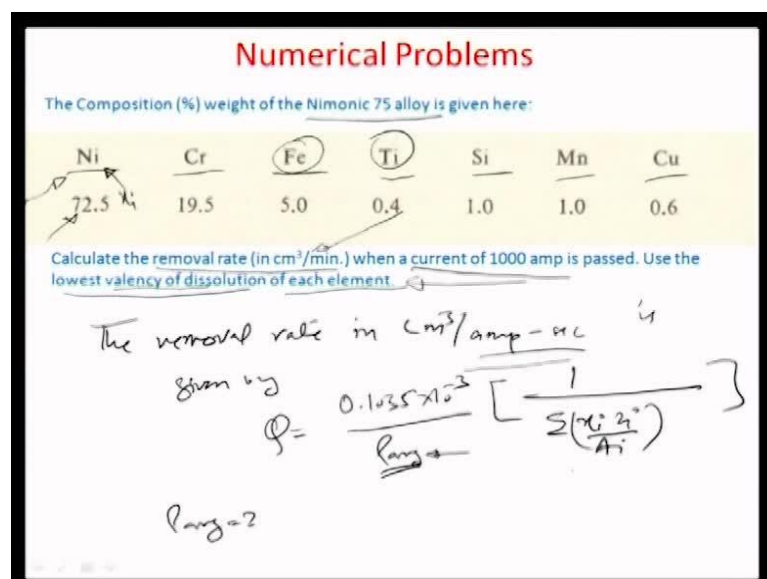
So, the theoretical predictions really do not take care off or do not count for, what is the valency state which is coming out of the ECM process. And therefore, you know sometimes the theoretically predicted rates may not tally very well with the actual rates. Actual rates may be slightly lower because of multiple valency states which may be coming out of such a system.

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So, that is what 1 aspect is all what has to be considered for any let us say electrochemical machining the other aspects of course, is the alloyed system as I told. And standard tables like these are very easy or very convenient to look at, you know in a nutshell what are the different states are of a particular material and how they will come out and also what is the corresponding equivalent density or a gram atomic weight of a particular material. And so these tables would be often on use throughout this lecture and even beyond for predicting some of the material removal rates from a fundamental stand point.

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So, now let us look at the alloyed system as I promised. So, we have a composition called nimonic 75 alloy here which is very often used. And ECM is performed often on. So, the composition is given right here in this table. So, you have all different phases in the alloyed system Nickel, Chromium, Iron, titanium, silicon, manganese and copper. And what these numbers are basically they mentioned about the different percentages of presence of this different states. Like this is corresponding to x_i for the Nickel state, this is x_i for the Chromium. So, called for the you know 5 percent is the amount at in which iron is present 0.4 present is in amount in which titanium is present so on so forth.

So, we need to calculate the removal rate in such a complex system alloyed system. Using the theory we have develop just now and the prediction has to be in centimeter cube per minute. The rate of material removal and the only thing given to us is that the current of 1000 amperes is passed and we want to use just the lowest valency of dissolution of each element. Although when predicting actual rates may be different because of as I told you multiple valence state coming out the dissolution process.

So, what do we do here? So, the first thing that comes to our mind is, what the material removal of an alloying system would be in, the removal rate as we just about derived and found out in the last 1 or 2 slides, in centimeter cube per unit charge ampere second is given by 0.1035×10^{-2} that is about 1 by the farad 96500 coulomb times the rho average. And this average is something we have to find out times of 1 by $\sum x_i z_i$ by A_i . And so this rho average is something that we need to determine for the particular alloy.

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Numerical Problems

W = weight of the electrode dissolved
 x_1, A_1, Z_1, ρ_1
 x_2, A_2, Z_2, ρ_2
 x_3, A_3, Z_3, ρ_3
 ...
 x_n, A_n, Z_n, ρ_n
 (Alloy of all phases i 's)

$\frac{x_1 W}{100}$
 $\left\{ \frac{x_i W}{100 \rho_i} \right\}$
 Total volume coming out = $\sum_{i=1}^n \frac{x_i W}{100 \rho_i}$
 Total weight = W

$\rho_{avg} = \frac{W}{\sum_{i=1}^n \frac{x_i W}{100 \rho_i}} = \frac{100}{\sum_{i=1}^n (x_i / \rho_i)}$

So, what is rho average and how do we determine it? So, the average density can be really found out by looking at, what is the total weight which is involved. So, let us say if w is the total weight of the electrode that is dissolved. And this w has components $x_1 x_2 x_3$ so on so forth percentagewise of materials with atomic weight $A_1 A_2 A_3$ so on so forth with a valency states, the lowest valency state $Z_1 Z_2 Z_3$ so on so forth.

So, therefore, the total amount of... and of course, the densities are $\rho_1 \rho_2 \rho_3$ so on so forth. So, the total amount of component corresponding to i equal to 1, which is present in this w , is essentially $x_i w$ or $x_1 w$ by 100, for i 'th component this $x_i w$ by 100. the total volume of the material which is present there is the total weight which is present divided by the density. So, the for the i 'th component the total volume which comes out coupled in this way w is basically $x_i w$ divided by $100 \rho_i$.

So, if I assume that, the alloy essentially composes or is composed of all phases i 's. We can say that, the total volume coming out is actually given by $\sum x_i w$ by $100 \rho_i$. Where i varies from 1 to n . May be there are about 1 phase or n phases of different materials and the total weight you already know is w . So, the average density can thus be recorded as the total weight divided by the total volume which is coming out, which is corresponding to i equal to 1 to n $x_i w$ by $100 \rho_i$. In just you know little simpler version can be 100 divided by $\sum x_i$ by ρ_i , where i can vary between 1 to n system. So, that is how the average density can be obtained.

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Numerical Problems

The Composition (%) weight of the Nimonic 75 alloy is given here:

Ni	Cr	Fe	Ti	Si	Mn	Cu
72.5	19.5	5.0	0.4	1.0	1.0	0.6

Calculate the removal rate (in $\text{cm}^3/\text{min.}$) when a current of 1000 amp is passed. Use the lowest valency of dissolution of each element.

The removal rate in $\text{cm}^3/\text{amp-hr}$ is given by

$$Q = \frac{0.1035 \times 10^{-3}}{\rho_{\text{avg}}} \left[\frac{1}{\sum \left(\frac{x_i z_i}{A_i} \right)} \right]$$

$\rho_{\text{avg}} = ?$

So, I would like to straight here that, in our case particularly because we have almost 78 phases as you can see here 1234567 phases, with different percentages and different of course, densities different atomic weight so on so forth. So, the total amount of row, in our case given by this 100 by $\sum x_i$ by ρ_i , can be represented as 100 divided by the first percentage that is percentage nickel 7572.5 percent. The nimonic alloy divided by the density of nickel which is 8.9 gram per centimeter cube plus that of the second phase which is chromium third phase is iron, you can see this different phase is here titanium forth silicon manganese and copper.

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Numerical Problems

$W = \text{weight of the electrode dissolved}$

x_1, A_1, z_1, ρ_1
 x_2, A_2, z_2, ρ_2
 x_3, A_3, z_3, ρ_3
 \vdots
 x_n, A_n, z_n, ρ_n

(At. wt. of all phases i 's)

Total volume coming out = $\sum_{i=1}^n \frac{x_i W}{100 \rho_i}$

Total weight = W

$\rho_{\text{avg}} = \frac{W}{\sum_{i=1}^n \frac{x_i W}{100 \rho_i}} = \frac{100}{\sum_{i=1}^n \left(\frac{x_i}{\rho_i} \right)}$

(Refer Slide Time: 29:10)

Numerical Problems

$$\rho_{\text{avg}} = \frac{100}{\sum_{i=1}^n \left(\frac{w_i}{A_i} \right)} = \frac{100}{\left(\frac{72.5}{8.5} + \frac{19.5}{7.19} + \frac{5.0}{7.86} + \frac{0.4}{4.51} + \frac{1.0}{2.88} + \frac{1.0}{7.43} + \frac{0.6}{8.56} \right)}$$

$$\rho_{\text{avg}} = 8.18 \text{ gm/cm}^3$$

$$Q = \frac{0.1035 \times 10^{-2}}{8.18} \times \sum_{i=1}^n \frac{w_i \cdot z_i}{A_i}$$

$$= 0.35 \times 10^{-4} \text{ cm}^3/\text{amp-sec}$$

So, is basically percentage of iron divided by density of iron plus percentage of the third phase, by density of the third phase plus that of the fourth phase, by density of the fourth phase plus fifth plus sixth plus seventh. And so the average density in this case, can be calculated as 8.18 gram per centimeter cube. So, once the rho average is calculated then of course, the material removal rate or the volume per unit charge that you may have already seen before, in can be determined as 0.1035 10 to the power of minus 2 by this rho average value. Which we have just calculated divided by 1 or multiplied by 1. Times of sigma xi zi by Ai and this i basically varies between again 127 in our case.

So, this can be written down here as 72.5 percentage xi equal to 1, times of the valency state the lowest valency state for nickel and in which it comes out is 2. We have to take the lowest valency state divided by the atomic feed of nickel which is 58.71 plus that for chromium plus that for the third phase plus that for the fourth phase plus that for the fifth phase sixth and 7th phases respectively. And if you really look at the overall value here, it comes out to be equal to 0.35 10 to the power of minus 4 volume per unit charge centimeter cube per ampere second.

(Refer Slide Time: 32:17)

Numerical Problems

$$P = \frac{100}{\sum \frac{w_i}{A_i}} = \frac{100}{\frac{72.5}{8.5} + \frac{19.5}{7.19} + \frac{5.0}{7.86} + \frac{0.4}{4.51} + \frac{1.0}{2.83}} = 8.18 \text{ gm/cm}^3$$

$$Q = \frac{0.1035 \times 10^{-2}}{8.18} \times \sum \frac{w_i \cdot z_i}{A_i} = 0.35 \times 10^{-4} \text{ (m}^3/\text{amp-sec)}$$

$$Q = 2.1 \text{ cm}^3/\text{min.}$$

Obviously, when 1000 ampere current is used the removal rate that is the amount of material coming per unit time is given by, what about this amount is times of charge per unit time or current. So, the q dot the material removal rate in this particular case, would come out to be equal to the current value which is 1000 amps. And we want to estimate the material removal rate in centimeter per unit. So, therefore, whatever value we have will have to multiply that by 60. So, this is charge per unit seconds and this would be charge per unit minute times of; however, volume whatever volume comes per unit charge which is 0.35×10^{-4} ; as you can see from here and this becomes 2.1 centimeter cube per minute.

So, again a very small amount corresponding to about a 1 kilo amp current and because it is a alloyed system, you have taken care of all the participants of the alloy. You know participating in the making the electrode in this particular system. And so therefore, this is the very nice way of estimating for particularly alloyed systems the material removal rate.

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Electrochemical Machining

•The relationship between the voltage applied across the electrodes and the flow of current is not very simple.

•The total potential profile consists of the following:

1. Electrode potential.
2. Overvoltage due to activation polarization. The electrochemical changes are in equilibrium when no current flows. The electrode potential acts as a barrier to a faster rate of reaction. So, an additional energy has to be supplied to get the required mrr.
3. Concentration polarization. The ions migrate towards the electrodes of opposite polarities, causing a concentration of ions near the electrode surfaces.

Each ion must pass through this concentration barrier to release its charge at the electrode.

4. Ohmic Overvoltage: The films of solid materials forming on the electrode surface offer an extra resistant to the passage of current.
5. Ohmic resistance of the electrolyte: The ohmic voltage drop occurs across the bulk of the electrolyte. This is the main voltage drop and is the only part of the electrolyte obeying Ohm's law.

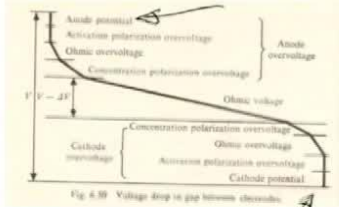
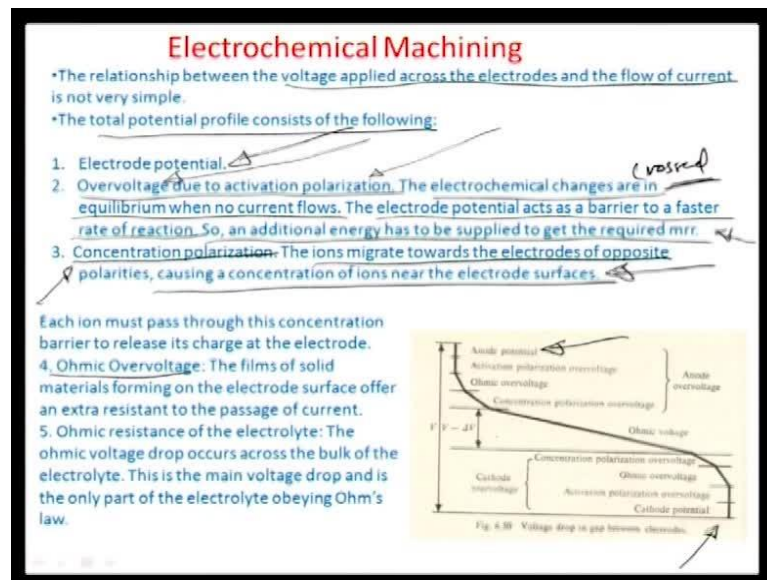


Fig. 4.39 Voltage drop in gap between electrodes

What I would now like to point out is again, you know something related to how the potential would get distributed between the cathode and the anode. Once it is made a part of the electrochemical cell and for doing that we need to somehow looking to the profile of the potential with respect to the inter electrode spacing or distance between the electrodes in such a system.

So, let us look at that in details. So, if you look at the way that potential varies from the anode side. In this case this is the anode potential to the cathode side. So, as I have already told before that, the work piece is made the anode and the tool is made the cathode, in this particular machining operation. So, therefore, the relationship between the voltage applied across the electrodes and the flow of current has a lot of you know effects due to which the potential may get changed. Particularly because of the formation of dual layer, particularly, because of the formation of migration, particularly, because of the formation of a resistive drop. This potential has substantial changes between 1 electrode and another.

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So, let us look at what all are the total components of such a potential profile which would be created. In meaning thereby, that what are the components which would cause, the potential would drop as coming from anode to cathode. So, 1 of course, is the overall electrode potential which is the anode or the cathode potential. The second component is a drop, which is because of a sort of activation polarization what; that means, typically is that the electrochemical changes are in equilibrium. When no current flows and there is a barrier potential which is also the zeta potential, we have developed a lot of formulations on this before and this basically is a barrier to a faster rate of reaction and this barrier has to be crossed.

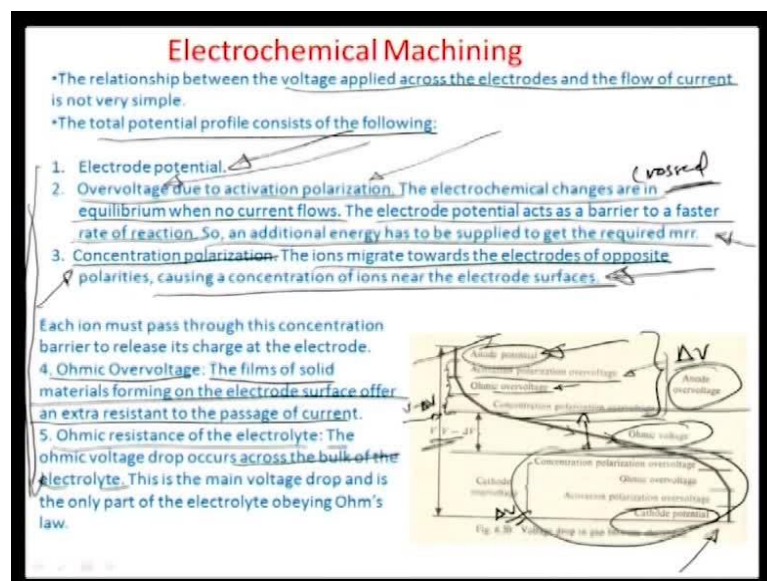
So, the zeta potential barrier which has been made has to be crossed, in order for the ions to start exchanging with the solution. So, an additional energy has to be supplied to get the required mrr. So, this is the over voltage therefore so whenever you are planning a certain voltage resulting in a certain current we will have to accommodate for this over voltages and supply a slightly higher voltage. So, that this losses can be taken care of, while doing electrochemical machining.

The second reason for potential drop is concentration polarization, which happens because ions migrate towards the electrodes of opposite polarities and there is a gradient of concentration which is created near any electrode surface. Because closest to the electrode the ion density would be the maximum and as you move away from the

electrode the ion density would minimum. So, there is always a concentration gradient and therefore, this creates a sort of polarizing effect, because there is a slightly higher density and a very low density and there is a gradient which is existing.

So, automatically there is a potential which is generated because of this sort of distribution of charges in a solutions space. And this also needs to be added on to the overall electrode potential because this is typically a drop and this drops needs to be given externally from the circuit. So, you have overvoltage due to activation polarization, you have a concentration polarization overvoltage which you are contributing to the overall design voltage that you are applying. And then of course, you have ohmic overvoltage, which is because of the formation of thin films of solid materials. As you know that, electrochemical process sometimes really very close to the electrode deposits a very small layer of metal.

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Although the purpose of the whole machining operation is to be able to immediately form precipitate from the debris which gets generated of the machining, but then 100 percent precipitation may not happen and there may be a small layer of, you know solid film which gets developed or generated which would create of course, a overvoltage effects. So, that is barrier has to be crossed it has a resistive drop component the potential drops down and that extra potential have to be supplied on to the overall design voltage that you are giving to the flow cell, electrochemical cell.

So, these overvoltages ohmic in nature, are because of films of solid materials forming on the electrode surface and therefore, an extra resistance would happen to the passage of current through this surface out of close to the surface. So, the ohmic resistance finally, plays a role also in the solution side and therefore, there is of course, ohmic resistive drop of the electrolyte itself, which would change majority of the potential function which is available from 1 electrode potential to the other electrodes potential. So, this is across the bulk of the electrolyte.

So, if you plot all these different potentials or reasons for you know, the potential drops reasons 1 to 5 in a plot and see how this potentials varies as you know the distance inter electrode distance or electrode spacing. So, you can see that this start with anode potential here and then there is a component which is added because of activation polarization. This is due to the formation of that stable layer which is also the zeta potential of the electrode surface. Then of course, the ohmic overvoltage which is sort of V equal to ir drop, the ohmic overvoltage is because of the thin films, solid films formulated at the electrodes extra depositions and then there is a concentration polarization overvoltage because there exist a gradient of concentration. And so that results in the whole anode overvoltage and then of course, the amount of voltage that is available to you at the end of all these after overwriting these potential functions or over overvoltage's is V minus ΔV .

Where Δv is an symbol of all these different overvoltage potentials. So, V minus Δv available here, now goes from 1 side to the other all the way to the cathode. So, the drop therein across the bulk of the electrolyte in this region is called the ohmic resistance of the electrolyte. So, there is a V equal to ir relationship again and then it goes to the cathode side in a similar set of Δv 's or overvoltage functions are met at the cathode side. Thus there is a equivalent V minus ΔV , which is formulated is the result of electrochemical machining.

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Electrochemical Machining

- If the total overvoltage at the anode and the cathode is ΔV and the applied voltage is V , the current I is then given by:
$$I = (V - \Delta V) / R$$

Handwritten note: $I = \frac{(V - \Delta V)}{R}$ Resistance of the electrolyte
- Where R is the ohmic resistance of the electrolyte.
- The conductivities of the tool and the workpiece are much larger than the conductivity of the electrolyte.
- The typical electrolyte conductivity is around $0.1 - 1.0 \Omega^{-1} \text{ cm}^{-1}$, whereas that of iron is $10^5 \Omega^{-1} \text{ cm}^{-1}$.
- Thus the surfaces of the tool and the workpiece can be considered as equipotential.
- The conductivity of the electrolyte is not really constant because of the temperature variation and accumulation of the bubbles.

So, that is how you can categorize the whole system of ECM therefore, the current which actually comes out now, because of the electrochemical transport is given by the design voltage minus the overvoltage per unit resistance of the bulk of the electrolyte. And R is the resistance of the electrolyte and we could have considered the conductivity's of the tool and the work piece, but they are simply much larger in comparison to that of the electrolyte.

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Electrochemical Machining

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- Thus the surfaces of the tool and the workpiece can be considered as equipotential.
- The conductivity of the electrolyte is not really constant because of the temperature variation and accumulation of the bubbles.

So, the overall resistance which really comes is because of the electrolyte and now, the solid metals. So, we really do not consider, we consider electrode to be a sort of potential sink or a potential source for charges. And we do not consider what happens within the electrode in terms of its own drops or own resistivity's. The conductivity's are simply too high, to be compared with the conductivity of the electrolyte solutions. So, whatever is the conductivity of the electrolyte is the standalone conductivity which is available for the purpose of calculation of current in electrochemical cell.

So, typical electrolyte conductivity's for example: vary between 0.1, 21.0 ohm inverse centimeter inverse and if on a comparative basis you compare the conductivity's of let us say iron, which can be an electrode it is about 10^5 . So, you can see there is a difference of about close to 10^5 to 10^6 in terms of the conductivity values. So, iron is not matter able, what is matter able is this conductivity.

So, the surfaces of the tool and work piece can be considered as by enlarge equipotential because the conductivity simply at too high. And the conductivity of electrolyte is not constant, rather it varies with temperature and as we will see later on we will have a design problem, where we will try to design the flow rates of the electrolytes flowing between a cathode and anode. And there you can find out that, how important or how critical temperature is. So, we will have to design the whole system based on whether the overall temperature of the system will hit the boiling point of the electrolyte, which is actually a design fault.

So, therefore, the conductivity varies truly with temperature and there is a relationship which gets generated. Because there is a sort of you know coefficient of thermal coefficient or temperature coefficient associated with the conductivity value of an electrolyte. And we will put that in place when we come to that those calculations and somehow try to see what or how, the mrr would be influenced because of these temperature variations of conductivity's locally to an electrode and may be into the bulk of the electrolyte.

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Kinematics and Dynamics of ECM

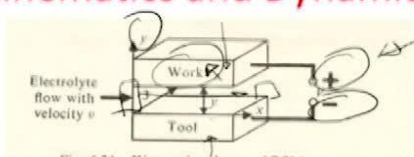


Fig. 6.31 Kinematic scheme of ECM.

- The figure above shows a set of electrodes with plane and parallel surfaces.
- The work (the upper electrode) is being fed with a constant velocity 'v' in the direction -y (normal to the electrode surface). The problem is considered to be 1-dimensional and the instantaneous distance of the work surface from the tool surface is taken to be 'y'.
- Considering the workpiece to be pure metal, the removal rate of the workpiece metal is given by $Q = AI / \rho z F$.
- If the overvoltage is ΔV , the density of the current flow through the electrolyte is given by:

$$J = \frac{K(V - \Delta V)}{y}$$

So, let us look now at a very interesting aspect of the how, the electrode and the tools would behave with respect to each other or in relation to 1 another, in terms of dissolution and in terms of distance change between both the surfaces. As I already mentioned the work piece in an electrolyte or in ECM process is, always made the anode thereby meaning it is connected to the positive potential and the tool is made the cathode connected to the negative potential. And in this particular system lets say, we are considering tool which is an electrode and the work piece, where work piece and there is a relative motion between the tool and the work piece in the y direction.

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Kinematics and Dynamics of ECM

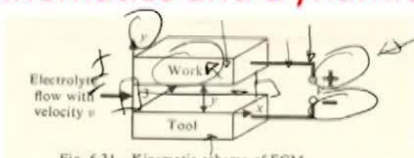


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- If the overvoltage is ΔV , the density of the current flow through the electrolyte is given by:

$$J = \frac{K(V - \Delta V)}{y}$$

Handwritten notes:

- $V = \text{Electrode potential}$
- $\Delta V = \text{Overvoltage}$
- $V = iR = \frac{\rho l}{K A} \left(\frac{Q}{A} \right)$
- $K(V - \Delta V) = \frac{Q}{A} \left(\frac{\rho l}{K A} \right)$
- $J = \frac{Q}{A}$

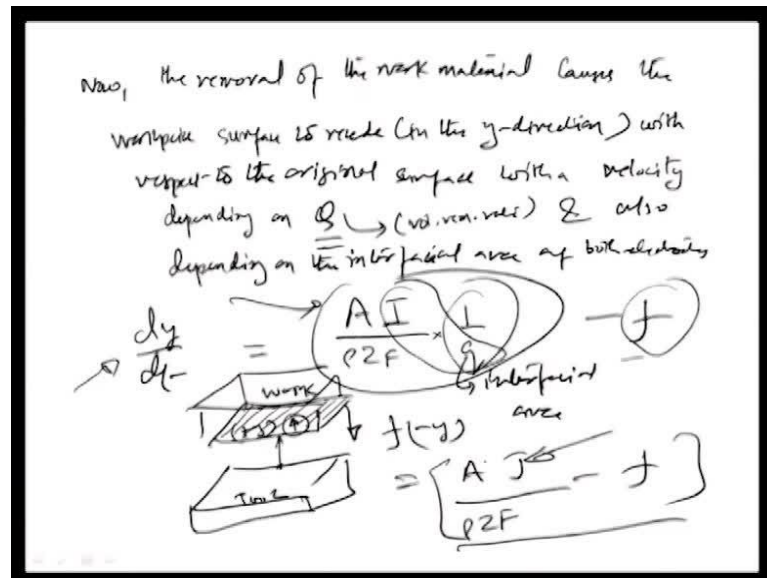
The flow of the electrolyte happens at a velocity V , from this end right here to this end. So, the flow is in this direction of the electrolyte. And we want to model how this system works because there would be a dissolution component associated with the work piece and there would be a relative motion between the work piece and tool. And so there should be some kinematics taking place between this dissolution which is receding away a surface and the approach of the work piece towards the tool.

So, in this case we are assuming that the work piece is moving towards the tool. So, the work is fed here with the constant velocity, if we call F basically the feed rate. So, we are feeding the work piece in the minus y direction thereby meaning that the work is approaching the 2 surface, the negative y direction. And we consider a 1 dimensional problem here and try to find out what is the correlation between the dissolution and the velocity. So, we already know that the volume rate of the removal of the material work piece material is given by A_i divided by ρzF , A being the atomic number i being the current in amperes, ρ is the density of the material to be removed z and F are the valency states and the faraday constant respectively for the work piece material. So, if the total overvoltage function which is available is ΔV meaning thereby that V minus ΔV is available voltage to us.

Then we have a relationship between the electric field and the current. So, you know that v equal to ir . And if we just manipulate it little bit we can write these as 1 by k , l by a where l is the length, A is the area of cross section k is the conductivity. And therefore, we can easily convert this into a situation where V by l which is also the electric field. Electric field is actually equal to i by kA and this i by a is nothing but, the current density j by k .

So, therefore, the j in this case can be represented as this V minus Δv , which is obtained voltage provide per unit the distance of separation between the work and the tool at any given instance of time let it be yt it is function of time. So, this is the field which is available and the local conductivity. Assuming the whole process to be done at a constant temperature right now that is for simplicity sake we would do that, comes out to be $k V$ minus Δv by yt . So, that is how the current density term in this whole electrochemical machining business would come out to be.

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So, now the removal of the work material causes the work piece surface to recede in the y direction. And this is with the respect to the original surface with the velocity depending on Q , the volume removal rate and also depending on the interfacial area of both electrodes. So; obviously, if you consider 1 dimensional motion, the volume removal rate per unit area of interface of the electrode would be nothing but, the velocity of recession of the surface because of the dissolution. So, therefore, we can easily say that dy by dt which where you have already seen before, why is really is this distance. So, distance between the work piece and the tool at a function of time

So, dy by dt becomes equal to the dissolution which is A_i by $\rho z F$ per unit area, let us say the area in this particular case is q some q . So, this is the interfacial area. So, that is how the surface is receding and this recession is in the opposite direction as the feed. Remember as we were talking about the 2 electrodes here, this is the work this right here is the electrode or the tool. So, work is being fed in this direction, minus y direction and the recession of the work piece surface is in the plus y direction, because of the dissolution.

So, recession is given by this term A_i by $\rho z F$ per unit area of this is the shredded area. The interfacial area of the of the 2 surfaces, F is basically the feed. So, this minus the feed is the total amount you know, still kind of going backward, which is the change of this y with respect to time dy by dt . So, I by q is current density vector J . So, AJ by ρ

zF minus f is how this formulation will look like. And of course, we already found out what this J value would be.

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The image shows a handwritten derivation of the kinematic equation for an ECM process. The derivation starts with the differential equation:

$$\frac{dy}{dt} = \frac{AJ}{\rho z F} - f$$

where A is the area, J is the current density, ρ is the resistivity, z is the valency, F is Faraday's constant, and f is the feed rate. The next step shows the term $\frac{AJ}{\rho z F}$ being rewritten as $\left[\frac{KA(V - \Delta V)}{\rho z F y} \right] - f$, where K is a constant, V is the voltage, ΔV is the overpotential, and y is the gap. This is then simplified to $\left[\frac{KA(V - \Delta V)}{\rho z F} \right] \frac{1}{y} - f$. Finally, the term in brackets is defined as λ , leading to the final equation:

$$\frac{dy}{dt} = \frac{\lambda}{y} - f$$

A handwritten note on the right side of the slide states: "Kinematic equation for an ECM process".

So, we can say that dy by dt equal to AJ by $\rho z F$ minus f can be written down as KA times of V minus ΔV divided by $\rho z F$. Where this KV minus ΔV by y is the current density vector minus f , if you pull out y of the whole term happens to be some constant times of 1 by y minus f , let us call this λ . So, we have dy by dt is equal to λ by y minus f and this is actually the kinematic equation for an ECM process.

So, we will investigate various cases of constants feeds or 0 feeds, in the next lecture today we are sort of coming towards the end of this particular lecture. So, we will in a nutshell, try to investigate how this y varies particularly when the feed is constant, when the feed is 0 feed or you know something where there is a definition of equilibrium gap which comes between this receding surface in the feed, when they equalize each other. So, we will look at those details in the next lecture.

Thank you.