Advanced Material Characterization by Atom Probe Tomography and Electron Microscopy

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Week-01

Lecture-01

Welcome to the first class of Advanced Microstructural Characterization by Atom Probe Tomography and Electron Microscopy. My name is Surendra Kumar Makineni. I am an assistant professor in the Department of Materials Engineering at the Indian Institute of Science, Bangalore. Okay, so before going to the topic, I just want to show you some of the reference texts which are very important for this course. The first part of the lectures will be on atom probe tomography, and the second part of the lectures will be on transmission electron microscopy.

So, these are the three books which are very important and will be very useful throughout the course lectures. So, the first one is by David J. Larson and his colleagues, where the book name is Local Electrode Atom Probe Tomography. There is another book which is a very useful resource related to the concepts of field evaporation and field ionization, and it is written by Baptist Galt and titled Atom Probe Microscopy. And the third book is Atom Probe Tomography: The Local Electrode Atom Probe, which focuses more on the construction of a LEAP, an advanced version of atom probe tomography, and some basics related to it.

In transmission electron microscopy, we have a very old book called Eddington, written by Eddington, and it is titled Practical Electron Microscopy and Material Science. And there is another book, Transmission Electron Microscopy by Professor Williamson Carter, and also another book, which is Electron Microscopy and Analysis, for reference texts. Okay, so as we know, we are surrounded by several materials, and our daily life always depends on them. For example, in construction and skyscrapers, we use a large amount of steel, including high-strength steel, so that they can sustain loads for a longer time.

Okay, and in automobiles and lightweight alloys, we usually use magnesium and aluminum-based alloys. These are typically for powertrain applications and also engine parts, especially the piston and the chamber, correct? So, the main thing is to lower the weight. And also to get it without any compromise on strength, correct? To sustain the loads during the operation of the vehicles or automobiles.

The third class of alloys, which are very important for defense applications and also for the aerospace industries, are called super alloys, okay? These are especially very important for high-temperature applications. In a typical jet engine, the turbine engine material has to sustain temperatures of about 1500 degrees Celsius. So, we use a special class of materials called super alloys. In rocket engines, we also use a large amount of super alloys, and another class is the copper alloys.

These are used for conductive applications to increase heat transfer, correct? These copper alloys should also sustain loads at very high temperatures, up to 300 to 400 degrees Celsius. So, all these materials have specific microstructural features, and as the course title says, advanced microstructural characterization. Correct? So, these are the microstructural features. Microstructural characterization by atom probe tomography and electron microscopy, fine?

So, we will go one by one. So, these microstructural features—what are these microstructural features? These are grains, grain boundaries, phases, precipitates, and defects. These all consist in the microstructure, which controls the properties. Properties can be anything—functional properties, mechanical properties, and magnetic properties.

But all these properties can be controlled by these microstructural features or by tuning the volume fraction of these features, and these features can be directly fine-tuned by studying the phase diagrams, solidification, and phase transformation. Correct—these are the three important things which are very important to design the microstructure. So, in designing the microstructure, we need the phase diagrams, solidification, and also the phase transformation. We will not go into the metallurgical aspects of these microstructural features.

Our main concern is how to characterize these microstructural features because these features ultimately control the properties. Fine? And especially, my area of interest is physical metallurgy and also the mechanical properties. Correct? So mostly, it will cover the mechanical response of these alloys. Now, characterization can be done, as I told you, by atom probe tomography. What is atom probe tomography?

It gives the chemistry. It gives the chemistry, fine? Chemistry means, what is the chemical composition of these microstructural features, fine? Electron microscopy gives the structure, fine? So, this structure is like an atomic structure, fine?

And these structures and chemistry are actually coupled. These are always coupled, fine? Fine, and due to this coupling effect, ultimately these two aspects control the properties of that material. Fine? The chemistry and the structure both— These are different for different microstructural features. So, for example, if you talk about grain boundaries, we call these grain boundary segregations.

And for phases, it can be a composition. For precipitates, these can be precipitate compositions, and they have a certain structure. which can be different from the matrix phase. So, here I am showing you some photographs—just a photograph of an atom probe located in ISE at AFMM, and also the microscopy, where both are located in the AFMM center in ISE.

An image where you can see this sequence of spheres, correct? And these aligned spheres are nothing but atoms which are aligned periodically, fine? And these are actually 100 planes. So, at each plane, you can actually visualize these atoms or get the chemistry at each plane. And here, on the right side, you can see the atomic column.

These are atomic columns. And this particular region which I am enclosing is one kind of precipitate. And you can see these precipitates, if you see these lattice planes, these are actually continuous. And this means these continuous planes, it is directly related to your what we call as a coherent precipitates. And these precipitates are very important because these precipitates actually strengthens the matrix.

strengthens the matrix and the interface between the matrix we call it as a this is a matrix this is a precipitate and the interface of the matrix and precipitate plays a very important role on the stability and the strengthening of the alloy okay so as I told you I have just briefly explained the microstructural features and here it is a very nice diagram where it shows this is the surface fine this is the surface at the right side and you can see at the surface this is a cross section cross section of the of a typical microstructure which we see underneath right so this is the surface and if you see that

We will have a grain boundaries. We will have a grains. Fine. These are the grains and we have a precipitates which is it might be inside the grains and it might be at the grain boundaries. We have in the microstructure can also contains voids at the grain boundaries and at the interior of the grains.

These grain boundaries. E are enclosing a particular region. So, this I am marking at the center and this one particular enclosed region is called grain. And this grain is nothing but a one particular oriented in a one particular orientation, crystallographic direction or we may tell it has a single crystal. and these single crystals if they are arranged in a random fashion correct you can see that these are randomly arranged this can be which are sharing the grain boundaries

which shares the grain boundaries so it means that if you go from this particular first grain to the second grain your orientation will change once you reach the second grain and these are called grain boundaries which are enclosing these grains, correct? So, this is typically a grain structure which we see in a typical microstructure. If you go little bit more details at higher magnification inside these grains, you can see that there might be a twins, there might be stacking faults. there might be dislocations inside the grains and ultimately these are the features which directly controls the overall property of any material.

If you go still in higher magnification at the atomic level, we can see that there might be the vacancies, there might be the atoms which are substitution atoms, there might be some interstitial atoms which can strain the lattice inside the grain. Due to that strain, it will directly impact the property of the material, especially the mechanical property, okay? So, this is the arrow mark which shows the scale where microstructural features at different length scales, correct? And these microstructural features directly controls, as I told you, electrical, optical, mechanical properties.

They also directly control the corrosion resistance, radiation resistance, hydrogen resistance which are very important for the hydrogen embrittlement effects in the microstructure. So, now what I will go through is briefly explain you the how a microstructure develops in a particular material, fine. So, if you consider there are these are the atoms which are arranged in a disorder. For example, if you can consider these as a liquid. And every element, if you consider one element, every element has a certain melting point, correct?

So above the melting point, it will have a liquid state and below the melting point, it will have a solid state, fine? So if you go below the melting point, these atoms will arrange in a certain crystallographic fashion, okay? So what they will do is first they will form a nucleus, right? So, the formation of these nucleus, it is a fluctuation process, correct? So, it is like for example, some of the atoms will come together, they will go and they will detach themselves.

But at a certain point, they will reach a critical size or critical where the atoms comes together. And they reach the R critical size where the crystal is stable. And this we call it as a nucleus. And this nucleus, what will happen? The more and more number of atoms will attach to that particular nucleus which is having a certain crystal structure.

And that is how this grows in a microstructure. So, we call this as a ordered arrangement of atoms. Now, if there is a liquid, if there is a liquid, now it might possible that the nucleus can These atoms can come together to form a nuclei at different locations. So, first location, second location, third location, fourth location, fifth location.

So, they can nucleate randomly at any place in the liquid. Correct? So, as I told you, these nuclei will convert to a certain crystal structure, which has a periodic arrangement of atoms. So, at each location, it develops a a periodic arrangement of atoms of the crystal.

So, this is crystal 4, this is crystal 3, this is crystal 2, and once this solidification is completed, what we get is a grain structure. So, here for the one, this particular grain corresponds to one orientation. This is the second orientation, third orientation, fourth orientation. So, this is how overall a microstructure develops, where these grains are surrounded by grain boundaries, and these grain boundaries have a misorientation—mostly more than 12 to 15 percent—these are called grain boundaries, fine.

So, it means that the crystal structure at grain 1—the orientation of the crystal structure at grain 1—is different from grain 2. Now, it means that if there are atomic planes in this direction in grain 5, at grain 4, these same atomic planes will have a different orientation. So, this is how the overall microstructure of the alloy develops. So, here I am showing you an electron backscatter diffraction pattern, where you can see that—we will not go into the details of this. But one thing to remember is the color—the orientation is directly related to the color, which is directly related to the orientation of the crystal.

It means that this particular big grain. The purple grain has one particular orientation, a crystal structure, and one orientation of the crystal. Fine? And this red color will have a different orientation. This green color will have a different orientation.

But overall, the crystal structure of the complete microstructure is the same. Only the orientation of the crystals is different. And these are surrounded by different grain boundaries. So, if you go to a particular grain, what we described here as a crystal, the atoms are arranged in a periodic fashion, fine? So, this is a particular unit cell, correct?

And it has certain lattice positions, and each lattice position is occupied by atoms. It is occupied by one atom, and if these atoms are arranged in three dimensions—X, Y, and Z—then you will develop a complete crystal or the grain for that particular microstructure. So, it is just a repetition of the unit cell with the atoms sitting at the lattice positions. Okay?

This is just a basic thing about how the microstructure develops, and in the coming slides, you will understand why this is important to learn about characterization techniques, fine. So, another important part—as I told you, as we discussed the crystal structure, correct?

and as I told you that these are arranged in a periodic fashion fine these are arranged in a periodic fashion the atoms are arranged in the periodic fashion now between the atoms in a solid there exists an interaction actually they can so these atoms are held together to form a crystal which is together so there is an interaction between these two atoms for example first atom and the second atom there is a certain interaction and this interaction is divided into two important concepts so one is attraction

And another wise is repulsion, okay? So, these are the two important aspects of the interaction between the two atoms. First, we call First, we discuss the repulsive force, okay? So, when atoms come close together, okay, what will happen? The electron cloud, the electron cloud The electron cloud of the atom will start overlapping. So, these electrons are negatively charged. So, what will happen?

These negative charges will develop a repulsive force, fine? And this repulsive force, okay, is termed as 1 by R to the power of 12, okay? And this equation is a famous equation by Sir John Lennard-Jones. He was a British mathematician in 1924. He found this equation, which explains the interaction between two solids or two atoms. Fine?

So, as I told you, the repulsive force is directly related to 1 upon R. R is the distance between the two atoms okay? And it is directly related to 1 upon R to the power of 12, which is related to the repulsive action. Similarly, there is an attraction. Okay. So, as the distance increases between the atoms, they have a certain mass, correct? Atoms have a certain mass.

And if two masses are present together, there will always be an attraction between the two masses, correct? So, when the two solids move away from each other, an attractive force develops between them, okay? And that attractive force is related to 1 by r to the power of 6, okay? So, there is a first variable which is called repulsive, which is 1 by r to the power of 12, and the second is 1 by r to the power of 6. Fine. So, these are the two forces which are very important to understand the interaction between the two atoms.

So, the attractive forces are directly related to, or what we also call, van der Waals forces. And these are very weak forces. Fine? These are very weak forces. Okay.

So, at very large distances, this particular equation is plotted here. So, this is your potential energy U. This is the distance between the two atoms. Fine? Now, this dotted line corresponds to the repulsive term. The lower dotted line, the dashed line, corresponds to the attractive term, the attractive energy.

And the resultant potential energy curve is this dark continuous line, which is the resultant of the repulsive and the attractive force between the two atoms. Okay? As I told you, these repulsion forces are directly related to the 1 upon r to the power of 12, and attractive forces are related to the 1 upon r to the power of 6. In this equation, there are two other terms, which are called sigma and eta. Fine? And what are sigma and eta?

So, if you see this resultant potential energy curve, you can see that there is a minimum point. There is a minimum point where the potential energy is minimum. Meaning, it is the most stable state at that particular distance of r0. Fine? So, if the two atoms are coming close together, then initially there will be an attractive force. Once they come closer and closer, there will be a position, a state where the potential energy is minimum.

And this minimum distance, which is maintained where the state has the lowest potential or the stable state, corresponds to R0. Okay, and this is also termed as the equilibrium distance. So, as I told you, in this equation, we have two terms: eta and sigma, and epsilon. We can call them as epsilon, eta, or epsilon, eta, and epsilon. And epsilon represents the depth of this potential energy curve. Okay?

So, it represents the depth, or we can say it represents the potential well. It represents the potential well of that particular energy, the potential energy curve between the particles, correct? And sigma, what is sigma here? Sigma represents the distance at which your potential energy, your U, is equal to 0, correct? So, this particular distance.

is related to sigma, fine, where the actual potential energy is 0, fine. So, now you understood this equation where this is the resultant potential energy curve, or it shows the distance which is maintained between the two atoms at the lowest potential energy state. Fine, and this dip corresponds to your epsilon, and the distance at which your potential energy U is equal to 0 corresponds to sigma, okay? And this model actually provides a useful way to understand the balance between the attractive and repulsive forces that govern the behavior of atoms and molecules in various physical and chemical systems. Okay, so we have briefly discussed the microstructure formation, we discussed the grains, we discussed the atoms which are sitting in the unit cell, and these unit cells are repetitive and they form a complete crystal state or the grain, and these grains are oriented in different orientations, correct? These, then they will have grain boundaries in between the grains. Now, this course is related to atom probe tomography to get the chemical information at the atomic scale.

So, we briefly discussed the atomic states related to the potential energy curve. So, about the Lennard-Jones potential. So, now before going to the main basics related to field evaporation and field ionization, which is the crux, which is critical to understanding atom probe tomography, we will briefly go over the history of the evolution of this technique. So, as we know, Professor J.J.

Thomson, in 1897, discovered electrons, which have a certain charge and mass. Professor Rutherford and his colleague Bohr—both of them—actually discovered the structure of the atom, correct? The structure of the atom means the electrons are in certain orbitals, which have certain energies, right? And the nucleus contains protons and neutrons, correct? Protons have an equal but opposite charge to electrons, right?

But they have a different mass than electrons. So, electrons are much lighter. But the neutrons, as the term suggests, are neutral. They do not have any charge. But their mass is similar to protons.

Correct? And here I am showing you the atomic structure of a carbon atom where the atomic number is 6 and the mass is 12. The atomic mass of 12 means there are 6 protons and 6 neutrons, which comes out to be 12. Fine? So, this is the structure of an atom which was proposed during 1911 and 1913. Later,

Professor Bragg described the atomic packing of these atoms in a certain crystallographic pattern, correct? In certain crystal structures. So, they provided the experimental confirmation of the atomic packing of atoms in crystals, correct? So, how these atoms are arranged in a periodic fashion. So, in 1928, there was a big development where Professor

Fowler and Nordheim, both of them, showed that by providing an electric field, by proving the electric field

we can actually strip out the electron from the atom. Correct? And this electric field requires a huge amount of voltage application. So, it is around 10 raised to the power 9 volts per meter that has to be applied, and such that the magnitude of, because of the magnitude of the electric field generated, we can actually strip out the electron from an atom.

Fine? So, this was the first time they predicted the magnitude. So, here I am showing you a sphere, okay, with a radius r, and if you apply a very high voltage, based on the radius r, it is directly related to the radius of curvature. Curvature and this particular R, so then the field, the electric field F, is directly equal to V divided by R. So, the smaller the radius, the higher the curvature.

Then, the greater the electric field generated around the sphere, correct? And at a certain voltage, for example, as I told you, they predicted around 10 raised to the power 9 volts per meter. If there is a voltage, then we can strip the electron from the atom. After this work, in the mid-1930s, Professor Gustav Hertz took on a PhD student named Erwin W. Mueller, whose main task was to design a field electron emission microscope. Okay, so as the name suggests, it is to generate a very high electric field such that the electron can be emitted and accelerated for imaging purposes, okay?

In 1936, Erwin W. Muller was the first person to design this FEEM microscope. What he did was take a tungsten element, and he sharpened that tungsten into a very fine needle, approximately 100 nanometers in size. And this is the setup. This is the schematic of the setup he used. So, this is a tungsten tip. Okay.

This is a very sharp tip around 100 nanometers. This is the phosphor screen. And vacuum, it was done under high vacuum. high vacuum and a very large potential of negative, negative potential was applied on the tungsten tip due to which at the phosphor screen, at the phosphor screen, he has recorded an image where you can see that there are four bright spots, diffused spots, correct?

And this tungsten needle was oriented in 110 crystallographic orientation. And due to this orientation, the tungsten has a BCC crystal structure and along the 110 direction, it always shows a two-fold symmetry. And exactly in this image where you see these bright diffused spots or the contrast, we can see that these are also a two-fold symmetry. Fine? Actually, it means that these are the electrons which are diffused.

They are recorded on the phosphor screen and accelerated on it, correct? With this microscope, he has achieved no more than 2-nanometer resolution, okay? But he was the first person to design this. FEM microscope. With this, we will end the first class. In the subsequent class, we will talk about how, by reversing this potential, a new field—FIM, or field

A new field, FIM (field ionization microscopy), has been developed by Mueller.