

Physics of Functional Materials and Devices
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Lecture – 13, Week 3
Alloys and Melts

Welcome to the final lecture of week 3. Till now, we have discussed mostly about synthesis protocols, why it is important to understand about various synthesis routes. Based on synthesis routes, we have seen that you can form materials and mostly we have been discussing about the case that you will always get an ideal material, but that is rarely a case in reality. Therefore, we have also discussed about the imperfections or defects which can generally stabilize in a material. The materials which we have been discussing are mostly solids. Let me ask you a very simple question.

Can you take any element from the periodic table and combine with any other element from the periodic table to make a material? Is it true? No, it is not. There are certain rules and observations based on which there are broad suggestions which have been made by scientists that suggest about the rules or conditions which generally lead to the formation of a stable material and also single phase material. What do we mean by single phase material, stable materials, how do you combine these elements to get a material is going to be one of the topics of today's lecture. We will start from discussing about alloys meaning when you take one element combine it with the other what happens and what you get.

So, we will start talking with alloys. Then, we will talk about the rules which are classified as Hume-Rothery rules that give you the broad descriptions of the required or desired conditions which will lead to the formation of stable alloys or materials. And, once you have those rules in mind you can go and try to make solid solutions and its types would also be discussed. What do I mean by solid solution? It basically means single phase materials. Then, we will go to random type solid solutions, primary and secondary types of solid solutions, what are substitutional solids and finally, before we end the today's lecture you will also understand about the interstitial solid solution.

Why? Because from the previous lecture you have seen that there are defects where which are very common and those defects are coming in because of interstitial impurities and if those impurities are actually going inside a solid, but the solid still remains stable then what types of solids are we talking about. So, those will also be discussed in today's lecture. An alloy is known to most of us and for this course the definition which we will be using is as follows. An alloy is a combination of a metal with at least one other metal or non-metal. This is the definition which we are going to follow during the course of this 12 week lectures.

Now, you have cases like metal-metal or metal-non-metal. Therefore, the alloy can be characterized as a metallic liquid or solid which will consist of combination of two or more elements. Now, what is the concentration of the metal or what is the concentration of the non-metal which is going to combine with the host metal? This is a fundamental question which can be asked and will come to your mind. Generally, one metal occurs in high concentration and this is called as the parent metal or solvent. So, you will have one of the components that will have higher concentration.

And what will happen to the element which is going to combine with this parent metal? This is going to be used as an alloying element or solute. Now, next question. What will happen when a parent material is dissolved in an alloying metal? Why should a material actually form when there are combination of two or more metals or a metal and a non-metal coming together? From the energy perspective, we know that every system wants to reach its minimum energy level. Therefore, which energy are we talking? We are talking about the Gibbs free energy. The system wants to be in a lowest Gibbs free energy state.

Now, when a parent material is dissolved in an alloying metal, what will happen? Atoms get displaced in the crystal lattice. So, you have mixing of atoms of two metals. So, what was the condition we had discussed earlier? You should have homogeneous mixing. That means, you have two types of metals if they are coming together, then you should have homogeneous mixing. That means, the environment around an element should be same throughout the crystal lattice, even if you move from one region to the other.

For example, if you want to make copper aluminum based alloy, it cannot happen that one region of the material is full of copper and the other is full of aluminum atoms. Then it is not a solid solution, it is a complex which is forming. You do not have a homogeneous mixing and that is why therefore, when you have a parent material being dissolved in an alloying metal, atoms will get displaced so that they can have a homogeneous mixing. They change their size as a function of composition of the solid solution or when you have mixing of two atoms taking place, what can happen? You can have a condition where a new crystal phase gets stabilized or when two elements are coming together, then what can happen? You get a new chemical formula. So, you have a new molecular unit forming or you can have clusters or super lattices that can form, but the formation of all these things are driven by the basic criteria which says that you must attain the energy minima condition.

So, what is a typical protocol which you use to make an alloy? You have a parent material or the solvent, then you have the alloying element or the solute, they are mixed. Please remember which of these two will have higher concentration? The solvent will predominantly have the higher concentration. Then you mix the solution and you let this mixture to solidify and you will get an alloy. The process of solidifications can be of different nature, can be driven by various protocols, but you need to move to solid

state and then you get an alloy. For example, if you look into the common alloys we talk about, you talk about brass, it is a mixture of copper and zinc.

Bronze, what is it? Copper and tin. Cast iron, iron and carbon. Stainless steel, iron, chromium and nickel. Let me give you an assignment for these cases which I have just discussed. Please find out which one is the parent material and which one is the solute.

And typically in examples such as door handles, statues, cooking pans and kitchen utensils, if you take the corresponding alloys, then what is the typical concentration of the parent and then you will find out the concentration of the solute. For the first three cases, it is easy to find out, but stainless steel if you change the concentration of the parent and the remaining solutes that means, the two remaining elements you will get different grades of stainless steel and hence you will find different grades of stainless steel in the market. Try to find out and you will understand it even further. So, let us start with the first concept that is can I choose any material and force it to work like a parent and then I choose any other element and force it to work it like a solute. It does not work like this.

Based on the observations, certain rules have been formulated by Hume and Rothery and therefore, the rules are called as Hume Rothery rules. These are set of four rules and mostly you will get the solid solutions that means, the desired single phase homogeneous materials if the alloying metal metal or alloying metal and non-metal follow these four rules. These are the relative size rule, the electrochemical rule, the relative balance rule and the lattice type rule. The relative size rule tells you the difference between these sizes of the alloying metal and the parent metal or alloying non-metal with the parent metal. This is written as consider the case where you actually calculate the size factor.

So, the size factor is defined as $1 + \frac{r_{\text{solute}} - r_{\text{solvent}}}{r_{\text{solvent}}}$ and it has been observed it is based on the observation. So, now, this is a general rule, but initially it was based on the observations that if the size factor is more than 1.14, it is unlikely that you will get a solid solution. But if you get the size factor less than 1.08, then mostly you get a single phase material or a solid solution can be obtained.

The next rule is the electrochemical rule. It states the more electropositive one of the materials is and the more electronegative the other one is the lower would be the solubility of the two metals. Therefore, if the difference in the chemical affinity of the two metals is large, the two atoms form a compound instead of a solid solution. So, if you do not have relatively same values of electropositivity and electronegativity, then you will not end up getting a single phase material. The third rule is the relative balance rule.

So, if you consider the alloying metal and the basic metal, they will differ in the valency that is the electron ratio. Hence, if you take the electron ratio which is the average of the valency electrons per atom, this will change as a function of alloying. Now, if you

want to have a crystal structure, for example, a perovskite type ABO_3 like crystal structure corresponding to a tetragonal Bravais lattice with space group $P4MM$. The crystal structures you can I just took an example, you can extend this kind of discussions to any crystal structure. These kind of crystal structures are more sensitive towards the decrease in the number of electrons than to the increase.

So, if you have materials where you have induced a case where the number of electrons will come down, then the possibility of the lattice having a stable condition reduces. This is the reason why a high valence metal dissolves a low valence metal poorly, whereas a low valency metal may dissolve a high valency metal quite well. So, what would be the condition you are going to take when you want to make a material? You would more likely take a case where you have the low valency metal acting as the parent and the high valency metal acting as a solute. And finally, you have a lattice type rule. Very simple to understand, only metals with identical lattices or structures are completely miscible that is they will form solid solutions. So, if you have elements for example, you have cases where the initial material which is being alloyed by another material, they have two different kind of lattices. For example, one has a cubic structure, the other has an hexagonal structure. It becomes highly unlikely that you will form a solid solution in this combination. So, if you want to have a stable material forming, then you would like to mix a cubic based material with a material which has a cubic lattice. I am still using the word highly unlikely rather than using that it will not form because these rules are indicative of the processes that would lead to unstable materials.

But it is not impossible that materials can be formed even when these rules are violated. And in today's laboratory or industries you will find that people are making materials which actually violate these rules and these kind of materials are quite regular in use. And such materials are actually being synthesized by varying more than one thermodynamic parameters. For example, these rules are mostly valid when you vary temperature as the driving force to induce the reactions. But if you take a hydrothermal route where you can change the pressure as well as temperature, then these rules can be violated and you can still get stable materials.

So, if you move from thermodynamic parameter temperature to varying pressure, then also these rule can be violated and you can get stable material. So, there are cases nowadays that you can form materials even when these rules are being violated. So, they are not as if they are the thumb rule, but they are just indicator and mostly they are true. As I said these rules are useful, but not compulsory. The solid solutions are what? These are homogeneous mixtures of two or more substances that exist in a solid state.

And you call it as single phase materials. These can be classified under two broad headings, these are random solid solutions or ordered solid solutions. The random solid solutions are the solid solutions where the solute atom are distributed randomly throughout the solvent crystal lattice. Resulting in what? Resulting in properties which are unique compared to what? Compared to the parent or the solute atom. So, when you mix two things you get a new property.

Ordered solid solutions in comparison to random solid solutions are the ones where the solute atoms occupy specific lattice site or sites in a solvent crystal lattice resulting in ordered arrangements. So, you will specify which Wyckoff position of the unit cell will the solute atom sit or occupy. They have long range atomic arrangement. Why? If you have ordered arrangement then automatically you will have long range ordering and they have unique properties because of this kind of ordered structures. The random solid solutions are further sub classified.

They can be classified based on the solute solvent composition. Again a question in a solid solution or an alloy which of the two generally have higher concentration solvent or solute? Yes, you are correct. It is the solvent which have the higher concentration predominantly in most cases. You can also classify or sub classify the random solid solution based on the solute solvent position. On the basis of the composition of solute and solvent you can have primary solid solutions or secondary solid solutions.

Similarly, based on the solute solvent position you can have substitutional solid or interstitial solids. I hope you understand the term substitutional that means, one of the atoms of the lattice is being replaced it is being substituted interstitial would be what? That you have an atom being placed in the interstitial site. Now, the composition of the homogeneous alloy is only possible within a certain limit. Sometimes it is called as the solubility limits. Solubility limits mean what? For example, suppose you have A atom combining with B.

So, what you can have you can write $A_{1-x}B_x$ where x denotes the concentration. Now, this value of x can vary from 0 to 1. So, if x is equal to 0 what do you get? You get A and if x is equal to 1 what do you get? You get B. So, this is the two end members of the alloy and intermediate would be your cases of alloyed solid solutions.

What do we mean? Within a certain limits. So, there would be a value of x where these materials would actually stabilize. Beyond that you would not get solid solution you may start getting compounds that is the basic meaning of limited range. In a primary solid solution the atoms of each elements are evenly distributed throughout the crystal lattice this we discussed and they do not segregate in different regions within the lattice. Therefore, what will happen? The primary solid solutions are often formed in alloys where the mixtures of metals or a metal and a non metal includes one pure component of the alloy. Let us take the example of brass where what are the two cases? Copper and zinc in their pure form.

Now, when you bring them together they will dissolve in each other to form a single phase alloy, but you have at least one pure component in this alloy. The secondary solid solution in contrast would be what? In such cases the alloying element is added to the base metal. In such quantities that the limit of solid solubility is exceeded. So, now, you cannot put tin inside the brass lattice you have exceeded that limit.

Brass lattice cannot exert more atoms from tin. So, but you are still putting in some more tin what will happen? They would lead to some segregation and you will get

secondary or intermediate phases. Therefore, in such secondary solutions you can find these secondary phases which can occur through the substitution of atoms in different elements in the lattice of the primary solid solution. And the secondary phase can be another solid solution. So, if you put more tin inside the brass lattice then you find that you have exceeded the solubility limit and then tin is forming certain ordered structure within the brass lattice. So, you have brass tin and a secondary phase based on tin if tin was acting as the solute.

And this extra tin may actually form another solid solution or it can find a case or induce a case where a chemical compound or a phase with the different structure is getting stabilized. And this is what happens in the case of brass alloys. The secondary solutions are classified on the basis of their structures. They are based on electrochemical compounds or you can have size factor compounds or you can have the electron compounds. Please now you can go back to your Hume-Rothery rules and you will find what is the importance of those rules and how those rules are used to understand the formation of these materials.

So, what would be the case for electrochemical compounds? These would be the ones which would obey the valency law and are formed by the combination of elements which are electropositive and electronegative. And then they have to follow the valency law of the Hume-Rothery process. Then you can have size factor. So, what would be the size factor compounds? Very simple. The component atoms in size factor compounds are closely packed and often have high coordination number and follow the size factor rule.

And finally, you have the electron compounds. Here in these materials, the electron ratio plays a crucial role in the stabilization of the phases and electron ratio is defined as the number of valency electrons divided by the number of atoms. So, you will find that these kind of compounds are formed at definite composition and they can vary as a function of structure of the crystal lattice. In comparison, the solid solutions can be either substitutional or interstitial. So, what would be the substitutional case? Here and the alloying atom or solute atom replace some of the parent atoms in the crystal lattice. So, if blue colored circles are representing the parent atom, then you will find that the solute atom is actually replacing some of the atoms which were there earlier when only the lattice was formed by using the parent atom.

So, you have replaced some of the parent atoms. This for example, if you take a brass alloy which is a mixture of iron and carbon, here the zinc atom substitutes some of the copper atoms. So, now you will get an answer to the question which I had asked earlier, which one acts as the parent and which one acts like a solute in brass alloy. The driving force is again to have systems which have lower energy that would make them stronger and harder than the initial case where only the lattice had the parent solution. Easily, you can now understand what would be the interstitial solids. So, you in the interstitial solids, you have the solute atoms usually in small concentrations and these solute atoms

are also small in size in comparison to the parent atom size and they occupy the interstitial site.

So, they do not replace the atoms, they sit at the interstitial sites. For example, if you take titanium alloys, you can have certain atoms which are going to occupy the interstitial sites such as oxygen, nitrogen or carbon and they will create certain bonding between the host atom and them and that would lead to the creation of stronger and more durable materials. And you will also have the case and which is mostly the case that alloys can consist of both interstitial and substitutional type conditions. One of the most common example is stainless steel which contains interstitially dissolved carbon together with the substitutionally dissolved chromium, nickel or some other metal. So, what would be the properties of the interstitial solids? You will have that only alloying elements which are small enough to form interstitial solid solutions and these are hydrogen, carbon, nitrogen or boron.

The lattice rule plays an important role in forming of interstitial solid solutions. The hydrides, the nitrides, the carbides and the borides of the transition metals are important groups of interstitial solid solutions. They are going to come in because you are going to have these kind of elements going inside the lattice of the parent atom. They find quite a large range of applications and you can just start talking about the different kind of steels which you can form by changing the concentration of the interstitial dopants. So, I hope now you understand the classification of alloys, what are solid solutions, what are random solutions, what are secondary solutions, what is the importance of forming these alloys and what are the rules which act as guide to decide the elements which should be brought together to form a new material.

And once you have these solid solutions, what are the ways they can be sub classified. These were the basic things which were discussed in today's lecture. In the next week, I will move on and we will start talking about the theory of solids. Why? Because we have understood the requirement of functional materials, we have discussed about the importance of having various types of synthesis protocols to get different types of materials, we have talked about the crystal structures of these materials, the defects and then how to choose the different elements so as to drive the idea of making new materials. Once that is done, you must understand what are the ways the properties of the materials change when we go from one solid to the other solid material.

In today's lecture, we followed the reference that is given in the book *Physics of Functional Materials* by Fredricksson and Akerlind and I thank you for attending this lecture. See you next week.