

metals 27 03 first cut

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We have a couple of times, actually, so we will essentially just begin to discuss age hardening. In particular, I mean, this is a general word, but typically it is a type of precipitation that happens in aluminum alloys, in some part, not in all aluminum alloys, but in a good size, in a good part of aluminum alloys. And we will discuss, essentially, we will discuss some general features of age hardening here.

So this is the typical heat treatment. What we need is always a phase diagram with a solvus line, something like this, where, essentially, decreasing the temperature, we have a decrease in solubility of the element B in A. So this must be the case. We will see that this is a condition that happens not only in aluminum alloys, and actually we discussed the other time, essentially, some systems where you can have age hardening, this type of precipitation.

And we also discussed that in reality, in different systems, you can have a large variety of different precipitates with different shapes, and also a different sequence of precipitates. What I mean by that is that you, if you look at the phase diagram, essentially, you have an equilibrium phase, typically here. This is a very generic phase diagram, just with a eutectic in the middle and the correct solvus line.

I think we'll see just in the next slide, essentially, a specific phase diagram for this case. But what I want to emphasize, essentially, in this phase diagram, the final equilibrium situation would be alpha, the original matrix, plus the precipitate beta, which is the equilibrium one according to the phase diagram. However, in many cases, in many systems, as you see here, you do not get, in this final equilibrium situation, in one step.

Very often, you go there, or you ended up there, but only after several precipitation steps. After, essentially, precipitating some intermediate phases, that you see, essentially, listed in here, and only after, at the end of the process, if you keep the process going to the equilibrium final stage, then you get the final phase, which is predicted according, essentially, to thermodynamic equilibrium and to the phase diagram that you typically refer to. There are, in between, essentially, some precipitates, which are metastable, but they form, so you can have the full sequence or, somehow, a reduced sequence, depending, essentially, on the condition of your heat treatment.

So, depending, essentially, on what is the temperature of this, in particular, this final stage here, and how long you keep the system in this condition here, this temperature here. Remember that here, essentially, this is just to get everything in a single solid solution alpha. Then you quench, so when you get here, this is a temperature as a function of time, so when you get here, after quenching, you have a supersaturated solid solution, so meaning, essentially, there is an excess of B atoms in the alpha solid solution.

This is also a metastable condition. The system cannot stay here forever. Sooner or later, essentially, it will precipitate something.

To speed up the precipitation and also to better control the precipitation, this is the most critical step. We have to carefully control the temperature and the time, the duration, of this critical step. And according, essentially, to that, to how we perform that precipitation step, we can have all these sequences or we can stop at a certain point, so we can have only partially the sequence of phases that you see here.

So, we will discuss in more detail the aluminum-copper binary system. So, this is an aluminum, essentially, alloy in which you put a small amount of copper. If you look at the full phase diagram, it is the one that you see is not really full, but it is, essentially, almost full.

It is up to, essentially, 35% of copper. The important region for us is, in reality, the one that you see here. So, typically, we have a few percent of copper, not so many.

I just put it up to this point in here because you see here the theta phase, which is the one that precipitates at the end of the precipitation stage, essentially, or steps, in this system. So, the final, we go, essentially, this is the solvus line we are interested in. We start from the alpha phase in the first, essentially, step.

We quench, and then we somehow leave the system for a certain time, and at the very end, but only at the very end, we expect to have the theta phase, which is copper-aluminum-2. So, as you see, this composition is, essentially, 33% of copper in aluminum, in atoms, percent in atoms. At the bottom here, you have the weight percent, which, obviously, is different.

So, this is just to show you that there is a theta phase in here, but the most important part of the phase diagram is, actually, the one here on the left. And we will concentrate, essentially, on this part of the phase diagram, which is, essentially, expanded in the figure that you see here. So, here, essentially, the thick lines, the continuous lines, are this part of the phase diagram, essentially, expanded.

So, here, this is the solvus line. Here, there is the region where you have alpha. Below this solvus line, you have alpha plus theta, the phase which, here, is somewhere on the right in this phase diagram.

Here, you have alpha plus liquid, and this is the liquidus line. Above this line, you have the liquid phase. You are, essentially, in here.

Okay? So, this is just an expansion of the phase diagram, essentially, that you see here. Plus, however, you see some dashed lines. These dashed lines, they are, essentially, some additional solvus lines.

Which, essentially, they tell you where these are metastable lines. They refer to a metastable situation. In which, but however, they tell you, essentially, below which temperature you can

have the formation of the metastable phases, which appear in this system.

Which are theta prime, theta second, and gT. So, we'll discuss more in detail what are these different precipitates, these different phases. In a while, but, essentially, this is what is the additional information that you can gather from this phase diagram.

So, essentially, what the phase diagram is telling you is that in equilibrium conditions, or in metastable conditions, depending on the phase, if you cross, if you go down slowly, and you cross this line, you expect, below this line, you expect to form the theta phase. Similarly, below this line, you expect to form theta prime. Below this line, theta second, and so on, and so forth, also for gT zones.

Okay, that doesn't mean that you have, again, in practice, in reality, the heat treatment that you apply is not cooling down slowly from the top. Because if you would do that, you would not get the best sequence of precipitation to maximize the mechanical properties of mine alloys. So, what I want here is, the objective here is to harden, to strengthen, aluminum alloys.

So, that is something that we need to keep in mind. So, I'll tell you, essentially, what are these, I'll tell you more details about the sequence of precipitation, but essentially, in one of the last slides, we will see that there is an optimal microstructure, which depends on the alloy and so on. So, essentially, there is an optimal combination between these phases, which is not the final one, typically.

So, you don't have to get to the end of this process. You have somewhere, somehow, to stop in here, to maximize the strength and effect that you can obtain with this treatment. And this is essentially why this is the heat treatment that has been crafted for this type of alloy.

So, here, this is just essentially the same heat treatment that you see discussed in here. You have just a few more details. So, you have now a specific temperature at which the annealing is done as a first step.

So, the T0 temperature in the previous plot is now 520 degrees. Then, of course, you quench to room temperature. Quenching is typically done down to room temperature.

And then, it tells you that essentially the precipitation step is done at 180 degrees. This is the typical temperature for this binary system. If I would change the system, if I would change the composition, everything essentially would be somehow different.

So, keep in mind that. So, if I apply this heat treatment with these specific, essentially, features to, in the aluminum cutter alloy, to an alloy, essentially, which has a few percentage, essentially, of cutter, this is essentially the sequence of precipitation that I will get, that I will observe. If I could observe all the steps at a microscope, I will see, essentially, we will start from α_0 , which is the super-saturated, sorry, solution, with an excess of, essentially, B in it.

So, this is retained, this is in a metastable condition. The first step will be the formation of what

are called GP zones, Vignet-Preston zones. The second step will be the formation of the theta second phase.

Then, theta prime, another phase, and finally, the theta phase. Notice that in each case, you have α , so this is essentially you will get the GP zones inside the α solid solution. So, α here has a different number in it, just to emphasize that the concentration of B atoms in α is changing.

So, when you precipitate the GP zones, some Kapper atoms, GP zones are richer in Kapper atoms, so some Kapper atoms will just migrate into GP zones, and the α , the surrounding α matrix, will be depleted of Kapper atoms. The same here, so the formation of theta second, which again contains more Kapper atoms, will deplete further the solid solution α , which will have a different composition, and that's why I call it α_2 , and so on and so forth. Actually, the composition of this solution, of the matrix, can be estimated from the solvus line that you see in that, because this is essentially another information, and here the solvus line tells you what is essentially the temperature, of which you can have that phase, but also which is essentially the maximum solubility in α of the element Kapper in this case.

So, at least it gives you a higher limit for this concentration that you see down here. Okay, let's now discuss... Yeah. No, okay.

Not exactly, okay. This is a good question, I am glad that you clarify, okay. Because, essentially, this depends on the composition, first of all.

So, if we have, I think, this sequence of phases, you have to set somehow a specific composition here. So, if I remember correctly, this is for 5, essentially, plus the weight percent. Okay, so let's assume we are here.

So, you go in this third step, you go essentially up to here. So, what you can form here, here you can form all phases, essentially, you are below every solvus line. So, that means that you can form θ , θ prime, θ second, and the GP zone.

You, the solvus line cannot tell you which one, cannot tell you which is the sequence, and neither which is the first one that will fall. Okay, that is somehow information which is related to how the nucleation happens, how the kinetics, how the growth is happening, and so on and so forth. So, this is something that you cannot infer from the solvus line.

However, the solvus line is telling you that if you apply, essentially, this first step here, this precipitation step at a higher temperature, or at a lower composition, you might not form these GP zones. For example, if for the same composition, if the first step, I do the first step at a temperature of 300 degrees, I am, essentially, above the solvus line of both θ second and GP zones. So, if I go up here, in this last step, the sequence will be, essentially, will be skipping these first two steps.

I will essentially go from the supersaturated solid solution to the formation of θ prime, because we are still below the θ prime solvus, and then to the final formation of θ . So, this is essentially

a kind of limiting, it's telling you some limiting condition. If you want the full sequence, your final heat treatment step should be below all the solvus lines. If you don't, I mean, if you want to skip some steps, okay, maybe you can go to a higher temperature.

Keep in mind that, in principle, of course, if you, when you go down here in the second step, you are freezing everything in the sense, so, the final situation, there is a supersaturated solid solution, which is thermodynamically not stable. So, if you wait long enough from a thermodynamic point of view, you will get to this final, stable thermodynamic state. But, as you know, I mean, the kinetics, especially at low temperature, the kinetics can be extremely slow.

And this is essentially why, in this system, to speed up things, essentially, you rise the temperature somehow, okay, so that the fusion becomes faster, atomic mobility is faster, and the reactions happens at a faster rate, at a faster, essentially, rate, which is essentially more reasonable, that you can investigate, and, even more importantly, you can use it in production. What I told you, essentially, about the discovery of aluminum alloys, of this H-atom phenomena, was exactly the, actually, didn't apply in this first step. It was an aluminum alloy, not an aluminum cathode, it was a ternary alloy, so the temperature were different from what you see here, but what they did is, essentially, they did an annealing, and then they, essentially, cooled down the system, so they did the first two steps, and then, as I told you, they stored the alloy somewhere, and they forget about that for a month, or maybe even years, I don't remember exactly, but for a long time, so they did nothing about that sample, they believe it was not good enough, but, inside the sample, the sample was, more or less, in this situation, so inside the sample, very slowly, so it took a very long time, but they got something, some type of, now you have to see the detail, but they got some precipitation of these phases inside the samples, even at room temperature.

It just took months or years. So, again, these are some typical conditions of exo-treatment, which can, in which you can observe this precipitation in a reasonable amount of time. Let's, essentially, now consider a little bit more in detail what are all these phases that formed.

So, the first one are, as I mentioned already, they are called Guinnet-Preston zones, from the two, essentially, researchers that discovered them. Not everybody agrees that this is a real new phase, because they are extremely small, essentially. These are, in the aluminum cutter systems, they are very small disks of the diameter of 10 nanometers, and even smaller is the thickness, which is only, essentially, two lattice planes.

So, it's extremely impractical. They are planes, they are, I mean, these precipitates, they are extremely small, especially along the thickness side. They, essentially, cover just two atomic lattice planes.

It's extremely thin. They form in a particular, with a specific orientation with respect to the matrix, the alpha matrix. So, you see, this is a sketch of the aluminum FCC matrix.

And the GPZ zone, essentially, they form like you see here, where horizontally, this is the

direction of the two 0-0 planes, in which, along parallel to which, you have the formation of this disk of GP zone. So, these GP zones, they are completely coherent with the surrounding matrix. Meaning, essentially, they form coherent interfaces.

So, there is good match between the interface, between this very small disk and the surrounding alpha matrix. However, there is a small misfit, essentially, originating from the difference, the difference between the lattice parameters of these zones and the lattice parameters of the original alpha FCC matrix. This, actually, there can be here some situations in which you have, you do not have misfit strain.

So, the match is relatively good or better. So, there is no misfit strain. By misfit strain, I mean, I think I can clarify it, I'll show you the picture, in the next, essentially, slide.

Okay? Just look at the picture in there. So, this is essentially the situation before any precipitation happens. So, you just have the FCC matrix, alpha matrix, all around is cubic, is FCC.

So, if everything is more or less perfectly, there could be some defects, but anyway, not in the region that we are considering. So, when you form the GP zones of any precipitate, in reality, because this discussion is more general, what you see, sorry, so, what you see is typically the new precipitate has a different density. So, it is either smaller or larger.

Suppose that it is smaller, like it is shown in the picture B. So, if it is smaller, you see it cannot occupy the entire volume that was previously, essentially, filled by alpha, by atoms in the alpha structures. So, there must be some strain in the lattice to accommodate for this difference, essentially, in the density which comes, which arises from the difference in the lattice parameters. So, this strain is represented, essentially, in the picture that you see here.

So, there are some bonds which are stretched, essentially. They are longer than they are supposed to be. They are, the angle can be slightly different, so they bend also, and so on and so forth.

This is what we call, essentially, misfit strain. And, to quantify that, essentially, we use, in case we do not have a misfit strain, we define, essentially, a delta parameter, which is just the difference between the lattice parameters of the precipitate, beta minus the lattice parameters of the matrix, alpha, divided by the lattice parameters of alpha. If there is some strain, this A beta prime here will not be exactly like this.

It will be, somehow, you see here, you imagine that there is the lattice parameters in beta, especially when beta is a particular mode, is somehow stretched. It is not the one that you expect when beta is isolated from the matrix, alpha, because of the strain, again. So, this is slightly different from the alpha beta that you find in here.

So, the lattice parameters of alpha beta prime account for, again, this misfit strain. Typically, the ratio, sorry, this is what we call epsilon, this new ratio accounting for the misfit strain, and this is typically, this is a rough estimate, it is two-thirds of delta. Delta is the unconstrained,

essentially, lattice mismatch.

So, this is essentially what we have summarized also in here, and the important point that later on we will discuss is typically the δg of strain, which, remember, it was a term which was present, essentially, in the nucleation theory, in the nucleation energy. So, this is typically proportional to the square of this δ here. So, somehow we can estimate δg s, basically, from the lattice mismatch.

If we know, and typically we do know, the lattice parameters of beta and alpha, we can have a rough estimate. A more, if you want, a more detailed equation for δg s, sorry, in the early slide I told you that it's proportional to this δ squared. To be more, to go more in detail, there are other factors that also appear in this equation.

One is the shear modulus g , which is the equivalent of the yarn modulus. The yarn modulus is in tension, the shear modulus is, if you apply, essentially, a force in a stress in shear conditions and not in tension. V is essentially the volume of the unconstrained pole, the volume, that is spherical, supposing that this is essentially a disk of Gb zone, of the Gb zone, looking from the top, essentially, we look at it from the top.

Not only that, but actually this δ , essentially, term, is also somehow correlated with a shape. This is a very empirical correlation, but at least for aluminum alloys, for this type of alloys, it is somehow correlated with the shape of the linear personal disturbance. So essentially, it has been found, this is the case of different aluminum and with something other, with another element, to form a binary system.

So aluminum cutter, for example, would be this one. This is just to show that this is the atomic radius of aluminum. This is the δ , estimated, essentially, from the atomic radius.

And then you see, basically, depending on this δ , you have that the Gb zones can be spherical in aluminum silver and aluminum zinc, or it can be a disk in the aluminum cutter system. Essentially, if this is higher than roughly 5%, you get a disk. If it is equal or lower than 5%, you get a sphere.

Again, this is an empirical, essentially, rule, but it might help, essentially, to rationalize what is happening here. Okay, so let's move on now. I mean, the Gb zones, essentially, they form first.

They are very small, extremely small, but as we mentioned, this is just the first step. If we move next, we'll have another phase, so the alpha is the matrix, the FCC solid solution, super saturated at the beginning and also across the different steps, and it gets the final equilibrium concentration only at the end of the process. The second, I'm sorry, the other phase that forms after the Gini-Emperor stone zones is the theta sector.

So this is a tetragonal unit cell that you can see, actually, at the bottom there, so in the picture that you see here, this is essentially the crystal structure of the alpha matrix. You see it's an FCC unit cell, a very simple cubic cell with all the atoms in the vertices and also in the center of each

phase of the cube. The lattice parameter here is 4.04 angstrom.

The tetragonal theta sector is the crystal structure that you see on the top here. So, if you notice, this is essentially a crystal structure which is very much related to the FCC.

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