metals 27 03 second cut

To the FCC structure of the alpha matrix. Why? How? So if you look at that, you can see basically that it is as we took two unit cells of the FCC alpha matrix. We put them one on top of each other.

Okay? We slightly somehow reduced the lattice parameters across the C axis, the vertical axis. So you see essentially that the base of the cube here is the same, 4.04 angstrom. It's the same as in the alpha matrix.

Both sides essentially. These are equal to the FCC alpha matrix. Not so along this direction.

So along this direction it is not twice what we would expect from the alpha matrix. Okay? It's not 80.08, it's something lower. So there is essentially, it has been short, it will shorten essentially along this direction.

Not only that, because in the FCC matrix essentially here, all the atoms are essentially equal. This is a random solid solution in which you have aluminum and catheter atoms which are randomly distributed in any position. In the tetragonal structure of the tetrasecond on the contrary, this is not any more disordered the occupation of each side.

As you can see essentially here, you have that aluminum atoms they are essentially at the bottom here of these structures, the black ones, and catheter atoms are on the contrary the white atoms that fill all the other half-planes, horizontal half-planes if you like. Okay? So there is a precise essentially an order of occupation of different sides in this tetragonal unit cell. However, you can understand that these two crystal structures are still very similar to each other.

On the base layer the lattice parameter is essentially the same, but even vertically the lattice parameter is very close to what we have in the alpha matrix. And this is why essentially the tetrasecond phase, this tetrasecond precipitate forms coherent interfaces along all directions, in all sides. You see the precipitate, essentially you see an example of a precipitate on the right here, but everywhere you see all possible planes 001, 001, 00 and 010 of these all planes.

They all can form coherent interfaces. Even the vertical ones with a little bit more strain, but of course they can still be coherent. This is also possible because the tetrasecond is bigger than GP zones, but still very small.

So this is the diameter of this essentially tetrasecond is roughly 100 nanometers. The thickness is also larger than GP zones, but it is still very small, only 10 nanometers. So these are still very essentially small particles.

Again, they can keep coherency with some strain along the vertical essentially directions. The

next step is actually the theta prime which okay, if you look at the Porter Easterling you will see that the structure is described as in this figure. To be to update somehow what is written in the Porter Easterling there has been essentially a publication in the literature where the structure has been better refined, so we know essentially a little bit more about this theta prime phase.

So the structure is very similar to what you see in the Porter Easterling book, but with a small difference in the position of the atom and in the lattice parameter. So it's not that far from what you see here. There is a small difference in this lattice parameter seen here and a minor difference in the position also of the atom system.

But essentially this theta second so theta prime phase is also tetragonal because you see that the base is still a square with a lattice parameter of 4.05 very close to the FCC alpha matrix. You have now a significant difference on the vertical axis of the C parameter, I mean larger than compared to essentially to the other theta second phase. So this is why essentially this phase typically forms semi-coherent interfaces in which as you remember because of the vertical essentially planes semi-coherence is essentially guaranteed by some dislocations or some other defects that appears once in a while to compensate essentially for the larger misfit that we have here between the lattice parameters of the precipitate and of the surrounding matrix.

So this is essentially the third phase that appears in this precipitation sequence when you get at the end the theta phase the structure you can see in here, this is correct in the Porter history book also it is at now essentially it is still a tetragonal unit cell but the lattice parameters now are completely different and are related to the one of the FCC matrix. So there is no way essentially this phase can match well at the interfaces, so all interfaces are essentially incoherent and the shape of this precipitate can be much more curved, I mean it can be very much different. So basically remember, because this is also important the theta second is all coherent, gp also is all coherent, theta second also is coherent, here it is coherent or semi-coherent depending on essentially the system, essentially in some system it can still be fully coherent, in some other system it is semi-coherent but only essentially along this plane this horizontal plane.

On the contrary, along the vertical direction, this already lattice parameters is too different, so the interfaces are essentially incoherent along the vertical essentially plane of the precipitate. And finally, in the case of the theta phase all interfaces are incoherent, there is no way here that we can form coherent or semi-coherent interfaces. I'm telling you I'm emphasizing here the coherency of the interfaces because this is important in the mechanical problems essentially maximizing again the mechanical problems.

We'll see basically that I mean, coherency you can understand that all these interfaces are somehow blocking they are hindering, they are somewhat preventing the motion of dislocations and hence they can strengthen my material which is essentially critical and we'll see that these precipitates have a different efficiency in improving the strength of aluminum atoms. So, here you just see, just to comment finally, you see essentially some micro-structures

showing you G is theta second, theta prime and the final situation with theta all surrounded by the alpha matrix. These are some examples essentially of micro-structures that you can observe essentially at the microscope.

Now, let's have a look of how we can actually understand this precipitation multi-step precipitation process from the point of view of the free energy of my system and how we can think of it as essentially an evolution through several metastable steps metastable stages which at the end, if you push it till the end, you will achieve essentially the final equilibrium conditions of my system. So, we can understand it essentially looking at a schematic which is just a sketch because it's not very easy to quantify and detail such a such free energy curve, but this is a sketch of, again, referring to the aluminum copper system of the free energy at a certain temperature, fixed temperature as a function of composition. So, here we have a copper composition and we imagine that my alloy is essentially this composition essentially corresponding to this point.

So, here we somehow have this is the free energy curve of the alpha FCC solid solution. The other curves that you see in there are the corresponding free energy curves for the other phases the other precipitates that can form Theta, Theta prime, Theta second and up there there is a curve in here which refers to the free energy of the GP zones. The reason why this is somehow connected with a dashed line to the free energy curve of the FCC alpha matrix is essentially because this crystal structure of GP or GP zones is extremely similar to the crystal structure of the FCC matrix.

So, I told you earlier that some authors consider essentially GP zones essentially an alpha an FCC crystal structure with a different composition, but the crystal structure is really very similar, extremely similar. So, for that reason, some authors essentially consider that this should be a single curve for the FCC essentially phase, FCC alpha phase. So, anyway, the point is that our starting point is, according to this energetic diagram, is alpha zero.

This is the super saturated solid solution after step two in here, this treatment. So, after I quench. When I quench, I get, basically, energetically the situation is what I see in here.

I am at this composition and everything is in a single phase. The alpha phase, the FCC matrix, which is super saturated. Now, if I wait long enough, again, in the first step I rise the temperature to make things happen a little bit faster, but essentially you see from this diagram that this, from the energetic point of view, from the free energy point of view, the energy of alpha zero is quite high.

So, you see immediately that the most stable point is actually the one given by the common tangent between theta and this point in here, alpha four. So, between the solid solution FCC with a very different composition of kappa and the theta phase. So, this is our final stage in thermodynamic equilibrium.

You see here all the intermediate steps that, depending on the practical condition at which you

make everything happen, they can take place or they cannot. I mean, the energy here is decreasing according to each step. Let me just essentially see that.

So, obviously, the very first step could be again, I underline that this is a possibility, but not always the case. It could be that just you see there is a common tangent between this part of the free energy curve that you see on the top and this point in here. So, essentially, if I move my system, if my system evolves from this point in here with energy g zero to this point in here with energy g one, which is on the common tangent here, drawn here, you see that you are already achieving a reduction in the free energy of the system.

So, obviously, there is a driving force to get from g zero to g one. But, of course, I can further decrease the free energy of my system. Essentially, the idea is the same.

There is another common tangent between theta second and the FCC solution here. You see that the tangent point in this part of the curve is changing and so is the composition of the alpha solution. And if I move, essentially, from g one to g two, this is referring, essentially, to a new equilibrium, essentially the second step that we were discussing, the second step in the precipitation sequence.

When you get there, this is essentially the free energy of my system when there is essentially the alpha matrix together with the theta second phase, the theta second precipitate. Next step, of course, will be in a very similar way moving to g two here, and this will be theta prime plus the matrix alpha alpha in composition alpha three and the final step will be to get to g four. So, thermodynamics essentially cannot tell you how you get from g zero, the highest energy point initially, that we have initially, to g four.

Thermodynamics is only telling you that g four is my final destination. I can go there in one single step. I can go there in several different steps, as you can see in here.

That is something that I cannot infer from this diagram. This is something that I know experimentally, that I can also understand from the point of view of nucleation and growth, and it depends critically on the temperature, on the composition of the system, and on the heat treatment essentially that I apply at the very last step. But, thermodynamics explains why you have this possible sequence of precipitation.

So, in every step, you lower the free energy of my system of a certain amount. So, every step is thermodynamically favorable, but the last step, getting to the last point, is the most favorable of all, and it will be eventually the final situation in which my system will essentially happen to be thermodynamic, with the lowest possible free energy. Notice that from this diagram we can also infer the compositions of the alpha matrix, the FCC alpha matrix, corresponding to the different metastable equilibrium at the different steps.

I told you that the composition in the initial step here, this stage here, the composition of alpha is alpha zero, which is also the composition of my entire system. But, when you precipitate

another phase, the other phase is always richer in copper, meaning that alpha is losing some copper, and the concentration of copper in alpha will, as you can see in there, will progressively decrease from alpha zero, alpha one, alpha two, to the final essentially concentration, alpha bow, and the alpha bow is essentially the concentration in which you have less copper than in all the other phases. So, why we have this sequence of precipitations? So the reasons here are complex, because they are essentially related to nucleation, to the nucleation and growth of all these different precipitates.

Essentially, depending on the temperature of your final step, the first step in the heat treatment, you can have a full sequence, as we already discussed, or, if you go to a higher temperature, you can have essentially just a partial precipitation sequence. Or even just, you can also just jump to the formation of a deeper phase. This is essentially what you see in this diagram.

This is the solvus lines, the phase diagram we saw earlier in the cathode-rich side, put together with a TTT diagram, which refers now to my, essentially, aluminum-cathode alloy, in this case. So, basically, what this is telling you, like I essentially already anticipated earlier, if your final step is done at a temperature essentially below all solvus lines, you will get this possible essentially to get the full sequence of precipitation. GP zones, then theta second, then theta prime, and finally theta.

And this is what you get if in the TTT diagram there is temperature here, but here there is time. So if I am, if I do my heat treatment here, remember the TTT diagram has to read at constant temperature, so I go down very slow, very quickly in temperature, then I, for example, I stop here, I keep the temperature constant, and here when I cross the first line is where a certain phase transformation begins. Okay? The phase transformation that begins, there should be a label in the TTT diagram that is telling you which is the phase transformation that begins.

So here you see that this line refers to the beginning of formation of the precipitation of GP zones. So when you cross this line, you form GP zones. If you keep the system at that temperature for longer, you cross another line.

This other line refers to the theta second phase, so when essentially you wait long enough, a certain amount of time here, you start observing the formation of theta second. And if you keep going, you see you cross another line where you begin forming theta prime, and here it is not shown, but essentially if you wait long enough, this line will go down for much longer time, at the end you will form theta. However, as I mentioned earlier, if I am, if my heat treatment is done at a temperature higher than this surface line, for example in here, for a composition like that essentially, so what you see is that here I cannot form essentially GP zones.

Sorry, sorry, the composition here in this plot was actually fixed on this vertical line, okay, so this is the composition we imagine corresponds to this TTT diagram. So if I am essentially at a temperature in between these two temperatures in here, you see I completely skip the formation of GP zones. I start as first precipitating theta second, then theta prime, and then

eventually theta.

And same for the other intervals. If I am essentially in between, just below the surface line, if I apply my heat treatment at the first step in here, I will essentially bypass all the other intermediate phases and I will immediately jump into the theta final equilibrium phase. Okay, this is not typically what we want to maximize hardness and strength.

To maximize essentially hardness and strength we want to have a more complex essentially sequence of precipitation. So we want something which typically starts with GP zones or at least theta second and somehow it stops also here, it stops before getting to the final formation. So why if I am at this low temperature I have all these intermediate precipitates? So the reason is, again, there are several reasons essentially explaining that, so not one not a single one.

It depends it is critically related to how the nucleation of these different phases happens and how the growth of these different phases happens. So we know several facts about what is happening here although some aspects might not be completely clarified. So essentially when you have a very low temperature and diffusion is low, atomic mobility is low it is easier to nucleate GP zones and GP zones typically there are some factors essentially which play a role here but typically for example GP zones form even when diffusivity is somehow relatively low like if you expect to be at such low temperature.

This is also something that can be enhanced to some extent by the presence of excess vacancies. By excess vacancies I mean that typically in any material you have a certain amount of vacancies which are essentially intermodal equilibrium because vacancies increase the entropy of your system even if they cost a little bit more energy because the presence of a vacancy implies that you have some you miss the possibility to form some bond between the atoms as they were in the perfect crystal. But again because you gain a lot of entropy, typically you have a concentration of vacancies in equilibrium in any material.

This concentration depends on the temperature in some cases, like in this case, if you cool down very quickly from high temperature where the concentration of vacancies is higher you can somehow freeze some vacancies inside your material. So you have an excess of vacancies with respect to what you would expect from thermodynamic equilibrium. This is what we call excess vacancies.

So you have essentially a larger amount, a larger concentration of vacancies with respect to what we would expect normally at low temperature. So this presence of excess vacancies that you get here because of the second step, because of the rapid quench that we apply in the second step typically favors the formation of GD zones. Also the GD zones themselves, once you have GD zones these are nucleation sites for the taste interceptor.

Essentially the interceptor typically nucleates, if you have already GD zones, nucleates more easily even at low temperature on top essentially of GD zones. And something also similar essentially happens later on. So theta prime typically do not nucleate on theta second phases,

theta second precipitate.

It nucleates on dislocations. Remember nucleation is typically easier on deep bed. In this case dislocation essentially helps reducing the misfit strain that is essentially accompanying the formation of theta prime.

Notice also here there is also a mechanism that has been demonstrated, which is somewhat similar also for other phases. When you form theta prime, so when you have a nucleation of theta prime here, so imagine you went through all the steps in here, so GD zones. Then you form theta second on top of GD zones.

So the GD zones somehow most of them appear. Then you start nucleating theta prime. So you form some theta prime precipitate together somewhere else than where before, some theta second precipitate.

So here the fact is there is a competition essentially for couple atoms between the two precipitates. Because they are both essentially rich in couple, richer than the matrix. So they both want, in order to grow they all need essentially couple atoms from the matrix.

So when you form the theta prime phase, which is thermodynamically more stable as we notice from the curve in here, so energetically theta prime is more stable than theta second. So essentially the growth the continuous formation of theta prime is essentially extracting, is stealing, if you want, couple atoms from the matrix and in turn from the theta second. Because if couple atoms will diffuse essentially in the matrix towards theta prime, there will be less and less couple atoms around theta second and this is actually making theta second essentially shrinking.

So the idea is essentially that after a while, theta second might even completely disappear. Finally, okay, these are just some other facts that theta phase nucleates on grain boundaries typically, or on interfaces between theta prime and alpha. So these solvus lines and this DT diagram, I already somehow discussed them and let me move essentially then to the conclusions here, which are basically what you can see depicted here.

So this is essentially these are some curves showing you basically the aging time in day together with the hardness measure because in one way we can measure hardness and essentially the bigger numbers the higher numbers, the harder is my material. So this is essentially, this plot refers to the last step in my treatment, so step number three here. Okay? This is just a typical temperature but as you notice here, I can change the temperature and if I change the temperature you see that these curves radically change.

If the temperature of aging is 130 degrees, you get the curves that you see there, where you also see that you get essentially a full precipitation sequence, GP zones theta second and theta prime. This is where you have GP zones and here is where you have theta second and then theta prime.