Advanced Materials and Processes
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Lecture – 22
Shape Memory Alloys: Case Studies and Applications (Contd.)

Welcome, to NPTEL; myself Dr. Jayanta Das from Department of Metallurgical and Materials Engineering IIT, Kharagpur. I will be teaching you Advanced Materials and Processes. Last couple of classes, we were discussing about shape memory alloys and shape memory effect, pseudo elasticity. Along this direction you may recall that we have classified various type of phase transformation and we have specifically discussed about martensitic transformation which is very much important phase transformation in order to obtain shape memory effect.

However, in case of a shape memory effect there are many different criteria has to be satisfied by alloy and different aspect has been already discussed; like reversibility of the phase transformation and from austenite to martensitic phase transformation, there is a requirement that the transformational strain should be accommodated by a specific twin variants only.

Because, once we cool austenite and the austenite transform into martensite, we deform the martensite and during that deformation one type of twin variant or twin type grows in expense to other and we can develop that strain which again recovered during heating because the whole martensite transform into austenitic phase and in this week we are trying to discuss more on some of the case studies.

Here, case studies means some specific alloy system and those alloy system what are the austenitic phase and what is their crystal structure, what is the martensitic phase and how they transform and what are their transformation temperatures and how we can tune those temperatures. So, these are the very important thing, so that we can develop specific alloy for some specific purpose. Also, ferrous system we have already talked and today we will talk about shape memory alloy in non-ferrous system.

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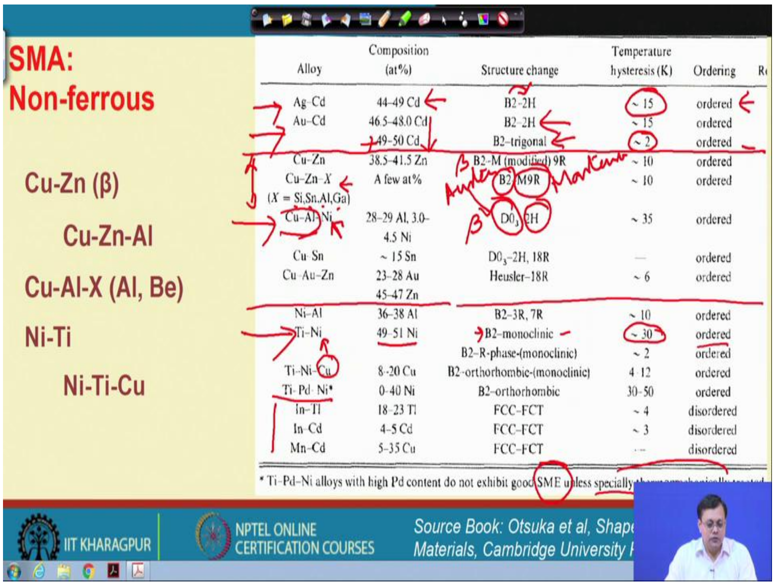

SMA:
Non-ferrous

Cu-Zn (β)
Cu-Zn-Al
Cu-Al-X (Al, Be)
Ni-Ti
Ni-Ti-Cu

Alloy	Composition (at%)	Structure change	Temperature hysteresis (K)	Ordering
Ag-Cd	44–49 Cd	B2–2H	~ 15	ordered
Au-Cd	46.5–48.0 Cd	B2–2H	~ 15	ordered
	49–50 Cd	B2–trigonal	~ 2	ordered
Cu-Zn	38.5–41.5 Zn	B2–M (modified) 9R	~ 10	ordered
Cu-Zn-X (X = Si,Sn,Al,Ga)	A few at%	B2 M9R	~ 10	ordered
Cu-Al-Ni	28–29 Al, 3.0–4.5 Ni	D0$_3$ 2H	~ 35	ordered
Cu-Sn	~ 15 Sn	D0$_3$–2H, 18R	—	ordered
Cu-Au-Zn	23–28 Au 45–47 Zn	Heusler–18R	~ 6	ordered
Ni-Al	36–38 Al	B2–3R, 7R	~ 10	ordered
Ti-Ni	49–51 Ni	B2–monoclinic	~ 30	ordered
		B2–R-phase-(monoclinic)	~ 2	ordered
Ti-Ni-Cu	8–20 Cu	B2–orthorhombic-(monoclinic)	4–12	ordered
Ti-Pd-Ni*	0–40 Ni	B2–orthorhombic	30–50	ordered
In-Tl	18–23 Tl	FCC–FCT	~ 4	disordered
In-Cd	4–5 Cd	FCC–FCT	~ 3	disordered
Mn-Cd	5–35 Cu	FCC–FCT	—	disordered

* Ti-Pd-Ni alloys with high Pd content do not exhibit good SME unless specially

Source Book: Otsuka et al, Shape
Materials, Cambridge University

Here, I show you table and if you kindly have a look, the first alloy system is the silver-cadmium, where the composition is lying around 50 – 50 or something like 44 to 49 % cadmium and the transformation occur from a austenite which has a B2 structure to 2H and the transformation hysteresis is rather small which is around 15K and this austenite itself is an ordered phase. So, this is something very interesting that the austenite here itself is an ordered phase. Why it is interesting because once it transform into martensite, those martensite should come back to its original or parent crystal structure which should be again ordered.

So, the direction of this transformation is important. I am talking about crystallographic direction. Now, in case of a gold-cadmium system very similar thing happens instead of silver-cadmium, the structural change is also similar; however, with certain composition range let us say from 49 to 50 it a transform to a trigonal type of structure here trigonal I am talking about a martensitic phase where it has a very small hysteresis and then it is also a ordered structure.

Now, the second category here which is very important is the copper-based system. So, copper-based system is very interesting because we all know about copper-zinc. 70 – 30 copper-zinc which is also known as brass, they are very soft metal and are very much useful for various engineering applications, but we can get this shape memory effect in a very different phase field. A different phase field means it has a β structure which occur let us say greater than 38 % and these β has a B2 structure which transform into a 9R type of structure which is a martensitic phase and we can also tune some of these transformation temperature by adding some amount of silicon, tin, aluminium or let us say gallium.

So, this is another very interesting copper base alloy system whereas, the second interesting copper base alloy system is on copper-aluminium system and here we purposely add nickel for some specific issues, we will discuss into detail. In case of copper-zinc the parent austenite has a B2 structure whereas, a modified 9R type of structure that is actually the martensite and B2 is the austenite. So, this austenite is a $D0_3$ which is also a ordered compound that appeared in a copper-aluminium, that phase also here called as a β phase and which transform into 2H type of martensite.

Now, similar thing also has occurred in copper-tin and copper-gold-zinc system; however, we will not be going in detail of copper tin. The third type of system which is also very interesting is a titanium-nickel system. So, here this is little off from a 50 – 50 composition where 49 or 48 to 51 nickel concentration. Here the austenite has again the B2 structure which transform to a monoclinic structure or sometimes there are some R phase also from we will go into detail of it and here the hysteresis is little bit higher and sometimes we purposely add copper to nickel and replace nickel in order to tune the transformation temperature once again and here B2 is also a ordered structure.

Then, titanium-palladium system is also important and there are some indium, cadmium and manganese-cadmium system. However, one should keep it in mind that some of these nonferrous systems required some specific thermo-mechanical treatment in order to gain the shape memory effect or good shape memory effect. A good shape memory effect means that deformation strain that is given to martensite can be reversed 100 % only after some training or can be given to the parent alloy.

So, these are some of the very important system that we have discussed and out of all the systems I specifically like to discuss this copper-zinc where β is the parent phase and aluminium is added to copper-zinc and the second system is copper-aluminium, where some amount of beryllium or nickel is added here, it is actually a copper, nickel, and aluminium system. And, the third system is the nickel-titanium and nickel-titanium copper is also another system.

So, all this we will go into detail of that and let us try to understand this matter.

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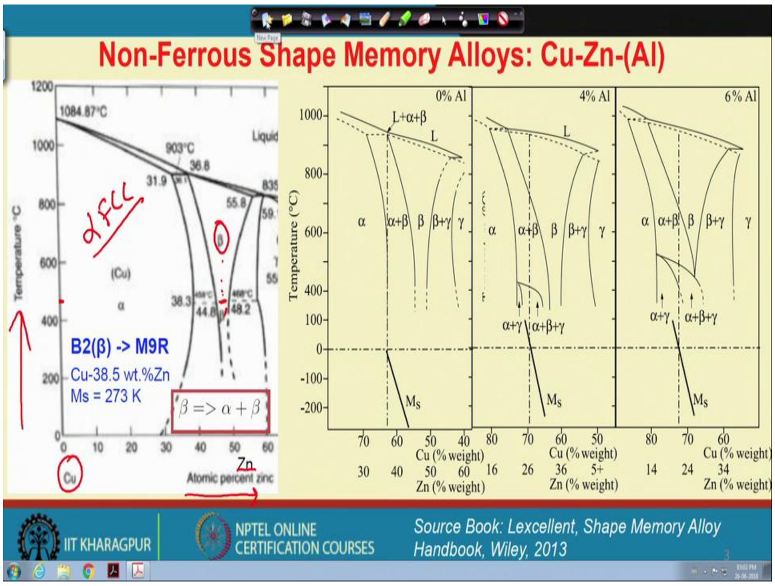

Non-Ferrous Shape Memory Alloys: Cu-Zn-(Al)

B2(β) -> M9R

Cu-38.5 wt.%Zn

Ms = 273 K

$\beta \Rightarrow \alpha + \beta$

Source Book: Lexcellent, Shape Memory Alloy Handbook, Wiley, 2013

Now, in case of a copper-zinc system if you look at the phase diagram of copper and zinc, this is an atom % of zinc and in Y-axis the temperature is shown here this is actually α FCC copper region, where we produce brass and here this is a very interesting, β phase that has a B2 structure and if we cool down β then around this temperature which is just somewhat about 450 °C to 500 °C. There, there is a transformation that occur from β to β'. Here, β' means that it is an ordered structure of β.

And, since β phase shows a shape memory behaviour then you can always ask why not to simply take such a composition, right? Unfortunately, β is a very brittle phase and there is no practical use of it. So, we have to develop alloys which contain β, but to gain some extent of formability we need help of this α. This means that we need a two phase structure and now how to get it two phase structure here. So, here this is a domain where α plus β will form.

So, I simply take this region and show it here with 0 % aluminum. Now, here the α phase lies, here β and you can have look that now if we have to produce such two-phase microstructure, I can choose some composition here or here and so on. So, this composition should go like here and now, if I go towards right hand side the problem arises that martensitic transformation is retarded and the transformation temperature goes down very below, how to read it? Here, you can have look that if I choose such a composition the M_s

temperature goes very down or even sometimes it does not occur at all. So, I have a very less chance to choose such a composition here.

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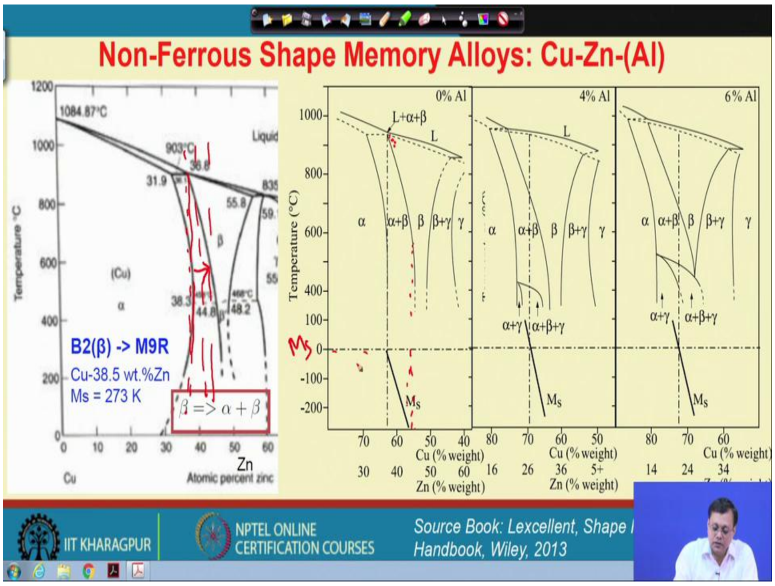

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Source Book: Lexcellent, Shape

Handbook, Wiley, 2013

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Or maybe if I need M_s temperature which should be somewhat around 0 °C and then I have to choose a composition which is here. And, for such a particular composition almost I get very less fraction of β and mostly I have α that is also another problem, because there is a transformation in this temperature range where β will transform into α plus β and the composition of β will be shifted to the right hand side, and of that β there will be no transformation at all.

So, in copper-zinc system this is a major problem; means if I choose a copper 38.5 wt. % zinc then the composition lies here and I may get a large fraction of α in order to attain a M_s temperature here; however, the β has a composition which will be shifted towards right where there will be no martensitic transformation at all and therefore, the idea came that whether we can tune this phase diagram in such a way that martensitic transformation temperature can be raised and we get a shape memory effect. And, therefore, people added 4 or 6 at. % aluminium and I show here with two different phase diagram with 4 % and 6 %.

Now, let us consider for the case of 4 % aluminium now you can have look here that if I choose such a composition purposely I will get M_s temperature this is actually the line which represent the M_s temperature. So, the M_s means martensitic start temperature. So, the martensitic start temperature lies around 0 °C whereas, on the other hand here if you just draw a tie line I will have a chance to get 50 % of α and let us say 50 % β and definitely during cooling, this β will be transform into β' and we will get a martensitic transformation and shape memory effect. So, problem has been solved by adding aluminium to copper-zinc system. So, this was the purpose of adding aluminium to copper zinc.

Now, in case of 6 % aluminium the situation is rather much better because I will have the chance to get a higher fraction of β and less fraction of α. So, the further improvement can be done. So, here M_s temperature lies around; let us say 0 °C and then the question arises whether we can add further aluminium or not, and that I will come into detail in the next slide.

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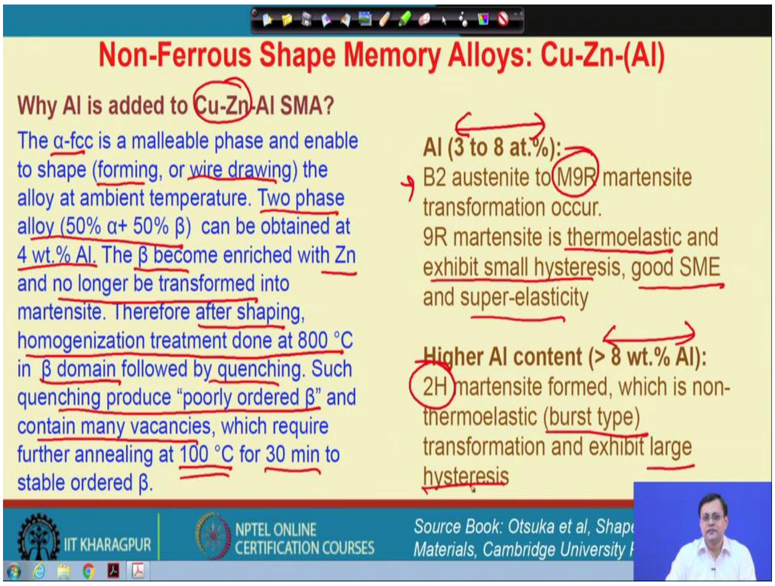

Non-Ferrous Shape Memory Alloys: Cu-Zn-(Al)

Why Al is added to Cu-Zn-Al SMA?

The α-fcc is a malleable phase and enable to shape (forming, or wire drawing) the alloy at ambient temperature. Two phase alloy (50% α+ 50% β) can be obtained at 4 wt.% Al. The β become enriched with Zn and no longer be transformed into martensite. Therefore after shaping, homogenization treatment done at 800 °C in β domain followed by quenching. Such quenching produce “poorly ordered β” and contain many vacancies, which require further annealing at 100 °C for 30 min to stable ordered β.

Al (3 to 8 at.%):

B2 austenite to M9R martensite transformation occur.

9R martensite is thermoelastic and exhibit small hysteresis, good SME and super-elasticity

Higher Al content (> 8 wt.% Al):

2H martensite formed, which is non-thermoelastic (burst type) transformation and exhibit large hysteresis

Source Book: Otsuka et al, Shape

Materials, Cambridge University

Now, the basic question that comes to our mind as I said that why we add aluminum to the copper-zinc system and what is the purpose of it. Usually, as I said that α FCC this is α copper phase which is actually the malleable phase and it enable us to shape the alloy during forming or let us say if I want to produce some shape memory wire like wire drawing process. So, the alloy at a ambient temperature, this allows some formability; however, the two phase region like 50 % α and 50 % β that I have produced around 4 wt. % of aluminum and this the problem with β. if β is very much enriched with zinc then there will be no longer any martensitic transformation, which you I show it here in the last slide.

So, therefore, after shaping we need to do some homogenization because during quenching itself some defect will be produced and defects means the large amount of point defect they are not good sometimes and. So, we need to homogenized around 800 °C in the β domain followed by quenching. So, during this homogenization and quenching treatment it produces poorly ordered β structure which is not desirable and it contain many vacancies and to anneal out or remove those vacancies from the poorly ordered β structure we need some tempering operation and heat treatment around 100 °C for some 30 minutes, so that we can get a very stable β which will be further transform into martensite and this is the basically purpose of adding aluminium.

Now, there are definitely some advantage and disadvantages of the system; however, people mostly preferred adding aluminium in the range of 3 to 8 %. Here a B2 austenite which is the β structure it transform into modified 9R type of martensite and this transformation is a thermo-elastic in nature. A thermo-elastic nature martensite has a feature that if you keep on cooling, the martensite nucleate and grow continuously, and this type of martensite usually show a rather smaller hysteresis and very good shape memory effect and very good superelasticity.

Whereas, if we go beyond 8 % aluminium then instead of these 9R martensite we get 2H type of martensite and the problem with 2H type of martensite is that it is not a thermo-elastic martensite or non-thermo-elastic martensite which occur by a burst type. So, and it exhibit usually a relatively larger hysteresis which sometimes may not be desirable.

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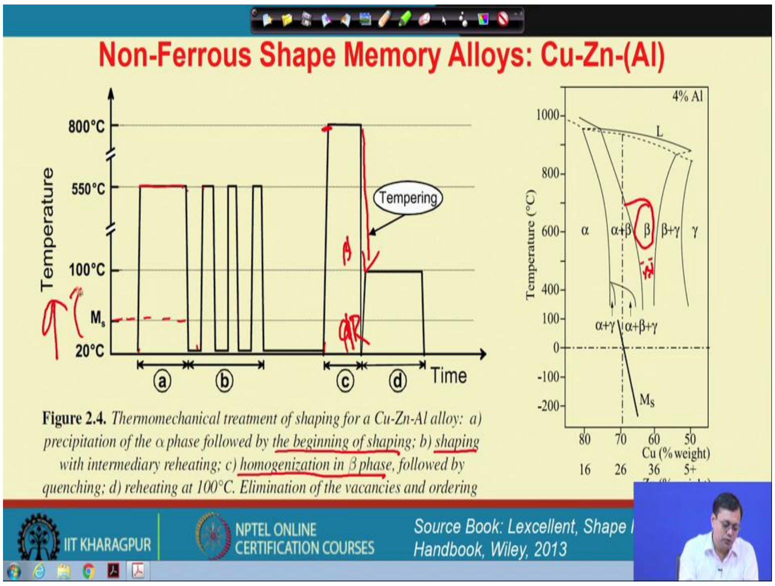

Non-Ferrous Shape Memory Alloys: Cu-Zn-(Al)

Figure 2.4. *Thermomechanical treatment of shaping for a Cu-Zn-Al alloy: a) precipitation of the α phase followed by the beginning of shaping; b) shaping with intermediary reheating; c) homogenization in β phase, followed by quenching; d) reheating at 100°C. Elimination of the vacancies and ordering*

Source Book: Lexcellent, Shape
Handbook, Wiley, 2013

So, I show you a schematic heat treatment process that show how really to develop this copper-zinc-aluminium shape memory alloy and how to process them. So, the treatment require let us say here this is a typical heat treatment schedule, that initially we heat it up to 500 °C. And let us say here we again heat and cool and heat and cool. So, this is where we begin the shaping operation and after shaping the alloy or wire drawing or typical shape we want to achieve. So, after the shaping has been reached then we go for some homogenization treatment of the β phase and therefore, we have to reach up to the high temperature β phase.

So, here this is the β phase. So, we are talking about high temperature means here, below this there will be a β' structure, please remember. So, once we cool it down then we get actually at room temperature and higher temperature we get β and then we basically get this 9R type of martensite and again the problem there that is M$_s$ temperature is somewhat in between 20 to 100 °C.

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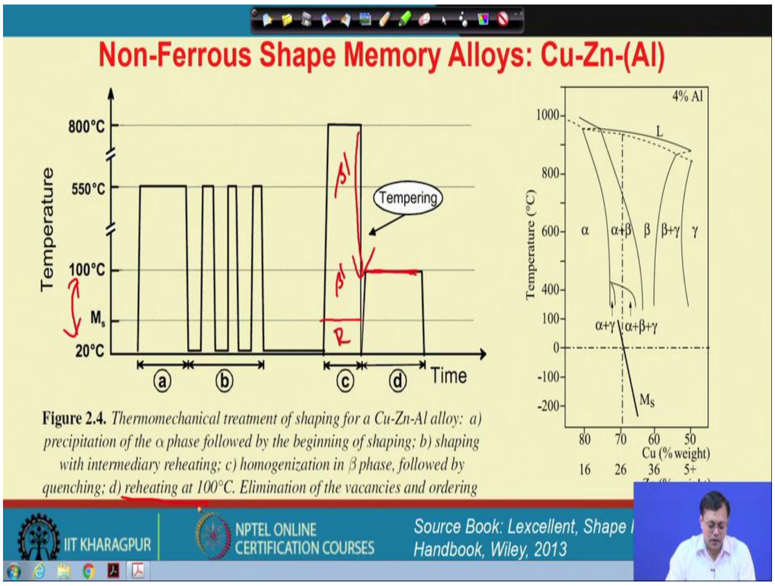

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Source Book: Lexcellent, Shape
Handbook, Wiley, 2013

Then if this M_s temperature is in between 20 to 100 °C and below there will be a martensite and here will be a β' and above there will be β. So, after initial quenching we need to go for some sort of elimination of the vacancies, this is basically done by a reheating of around 100 °C.

So, this is one very specific treatment that copper-zinc-aluminium system require. So, here just as a schematic I show you that β which will appear here and β' will appear somewhere here this is β' and here will be the 9R inside.

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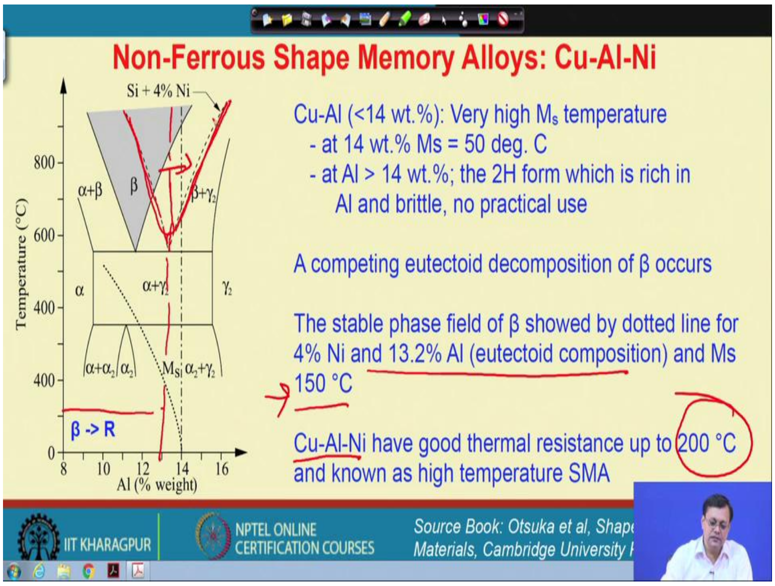

Non-Ferrous Shape Memory Alloys: Cu-Al-Ni

Cu-Al (<14 wt.%): Very high M_s temperature
- at 14 wt.% Ms = 50 deg. C
- at Al > 14 wt.%; the 2H form which is rich in Al and brittle, no practical use

A competing eutectoid decomposition of β occurs

The stable phase field of β showed by dotted line for 4% Ni and 13.2% Al (eutectoid composition) and Ms 150 °C

Cu-Al-Ni have good thermal resistance up to 200 °C and known as high temperature SMA

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Source Book: Otsuka et al, Shape
Materials, Cambridge University

Now, the second system that we are interested to talk about is copper-aluminium-nickel system, once again here the phase that shows shape memory behaviour is the β phase again. Here I show you a phase diagram with copper and aluminium. So, please consider the β phase field to be the dark region only and the martensitic transformation temperature varies with the aluminium content and therefore, the M_s temperature is shown here. This means if we increase the aluminium content then M_s temperature actually decreases very fast. Now, what are other problems please have a look.

So, the M_s temperature in this region is quite high and just by adding 4 % aluminium it goes to 0. Now, let us assume that we may have something like 14 wt. % then M_s temperature is around 50 °C. On the other hand, there is a competing eutectoid decomposition, how to read it here the β will decompose into α and γ_2.

So, there is a eutectoid decomposition which occur in competition with the martensitic transformation and therefore, we have to tune the alloys. So, that these eutectoid decomposition must be retarded and martensitic transformation should be enhanced. This means in a TTT diagram we must develop in such a way that the transformation way should move to the right hand side for eutectoid transformation and therefore, it has to follow in such a way.

So, once again, I just summarize the case here that in copper-aluminum, aluminum less than 14 % has to be chosen and if we go for higher concentration of aluminum then 2H type of martensite will form and it is very brittle and there will be no practical use. However, the stable phase field of β, which is shown by the dotted line here, can be obtained by adding some amount of nickel. Here, nickel is purposely added here, so that these phase field will move here. What will be the benefit of it? It will retard the eutectoid composition and the M_s temperature is around 150 °C, we can obtain.

On the other hand, this particular copper-aluminium-nickel system is very good because the Ms temperature is quite high and we can use it as a high temperature shape memory alloy and. So, we if we have to develop such a shape memory alloy where the martensitic transformation is also somewhat acceptable and we will get a large β phase field and this is one of the very interesting phenomena in case of a copper-aluminium-nickel system.

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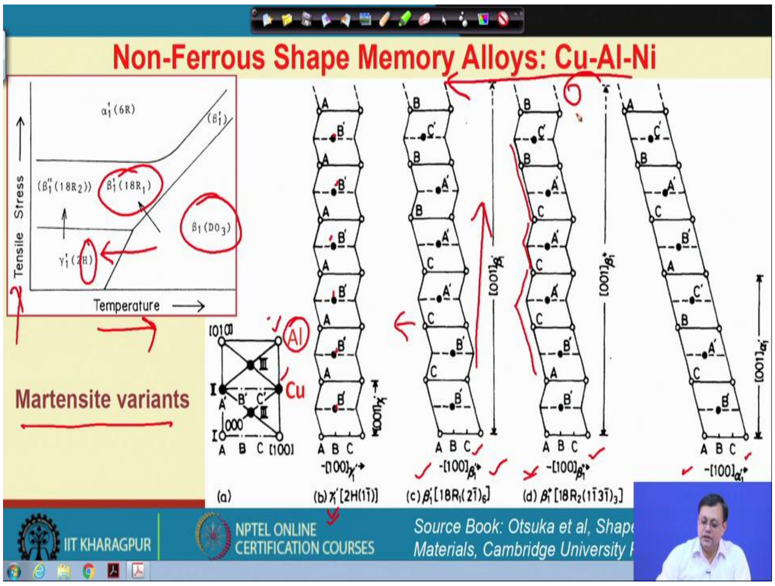

Non-Ferrous Shape Memory Alloys: Cu-Al-Ni

Martensite variants

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Source Book: Otsuka et al, Shape

Materials, Cambridge University

Now, in case of copper-aluminium-nickel system, we should look at some of the variants that appear. The martensite variants are important because we know about the crystallographic changes that occurred in this particular case.

The β phase which is mentioned has D_{03} structure, which transform into 9R or 18R type of martensite. Now, here this is a stress versus temperature axis. In case of a transformation, which may also depends on a higher aluminium content the H or hexagonal phase martensite may also be formed. Please have a look at different variant, which is shown here as a β', β" and α' structure. These are different variant of the martensite and the difference stacking sequence are shown here, where the empty bubbles represents aluminum and the filled bubbles are the copper.

So, these are the position of the copper atom and we introduce some stacking fault inside it, so that we get the martensite variants of β' structure here it is β" and it is α'. So, this is along the direction of <001> β' type of structure. So, all these structures are very much important in order to accommodate strain because once we deform along this direction then the strain can be accommodated by introducing the growth of one type of twin and fault in the structure. So, this is let us say the stress direction or shear stress direction along one of the direction.

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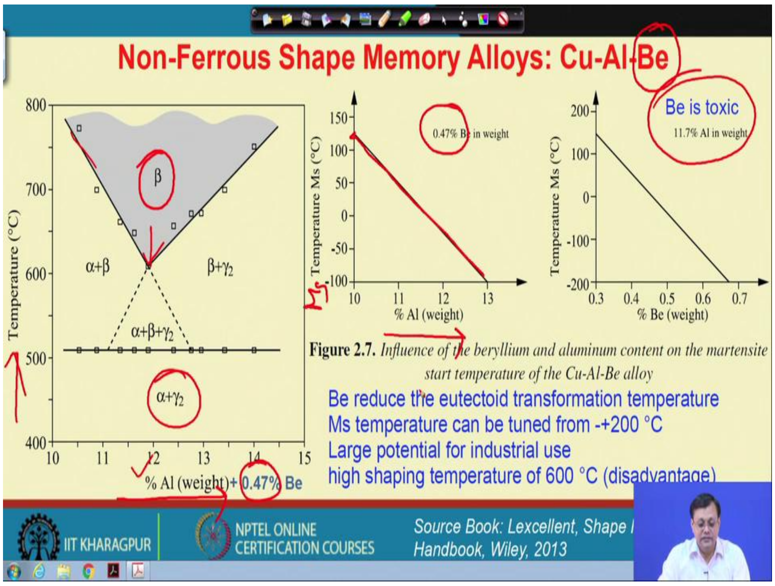

Non-Ferrous Shape Memory Alloys: Cu-Al-Be

Be is toxic

Figure 2.7. *Influence of the beryllium and aluminum content on the martensite start temperature of the Cu-Al-Be alloy*

Be reduce the eutectoid transformation temperature
Ms temperature can be tuned from -+200 °C
Large potential for industrial use
high shaping temperature of 600 °C (disadvantage)

Source Book: Lexcellent, Shape
Handbook, Wiley, 2013

Now, the third alloy system that is very much interesting to us is the copper-aluminium and beryllium alloy system. One should keep it in mind that beryllium is very toxic. So, initially the system itself could be used for industrial purpose, but it cannot be used for any kind of replacement of bone or any kind of bioimplant material. And, here also again a β phase, which could be transform into a complex type of martensite structure and the phase diagram is shown here in case of aluminium percentage and specifically for 0.7 % beryllium.

So, this is the β phase field and which will transform to α plus γ_2. This is similar eutectoid transformation in case of aluminium system that I have discussed just couple of minutes ago. So, if we choose 0.47 % beryllium wt.% you can see that the martensite start temperature keep on decreasing by adding aluminium content, if we increase aluminium content means if I go into this direction whereas, if I keep the aluminium content as a fixed. So, here aluminium content is fixed and M_s temperature can be tuned from let us say something like 200 to -200 °C, this is a huge range.

So, if I want somewhat like a 0 so, 0.7 % of beryllium, it will give us something like 0. So, the benefit of these copper-aluminium and beryllium systems, basically beryllium can be added to tune the M_s temperature by alteration of aluminium and beryllium content. On the other hand, beryllium has a large help and it assist such that eutectoid transformation temperature can be further reduced. So, this transformation could be retarded. So, we can get martensite very easily and another advantage is that martensitic start temperature can be tuned plus minus of 200 °C by very little fluctuation of aluminum or beryllium content.

So, this also help for a large potential for the industrial use. Also we need to shape this alloy above 600 °C because to avoid formation of beryllium containing compound. This is a general disadvantage. So far, we have discussed two major system; one is copper-zinc, another one is copper-aluminium.

In case of copper-zinc we have seen that we need to add purposely some amount of third element, so that we can tune the transformation temperature, very similar way, in case of copper-aluminium system we need to add beryllium or 4 % of nickel, so that we can tune this transformation temperature in order to get the desirable phases. So, in the next case studies we will be discuss and continue in the next classes.

Thank you.