Advanced Materials and Processes
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Lecture - 23
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, this week we were discussing about various case studies of Shape Memory Alloys. The case studies means, that different alloy system that exhibit the shape memory effect and pseudo elasticity. So far, we have discussed about ferrous alloys and non-ferrous system in non-ferrous system, two important system has been discussed, one is copper-zinc and other one is copper-aluminium.

So, in copper-zinc system we purposely add some amount of other alloying elements so that we can tune the transformation temperature, very similarly, in case of copper-aluminium system we purposely add nickel and some amount of beryllium, so that we can tune the transformation temperature means, M_s temperature. Among all the very important non-ferrous system titanium nickel plays a very major role as the shape memory alloy because of its applications, because it has a very wide range of application and we will go into details of it.

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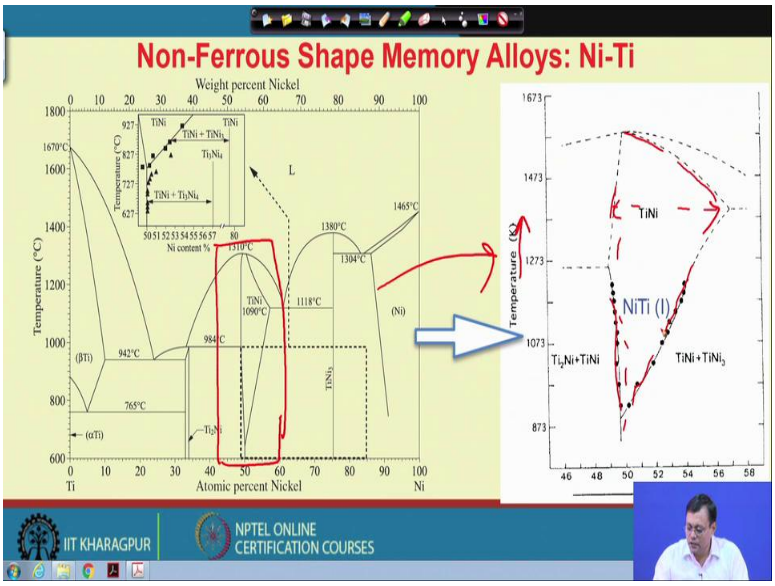

Non-Ferrous Shape Memory Alloys: Ni-Ti

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So, let us start today’s discussion with the nickel-titanium system, before going to different phase transformation in nickel-titanium, we must try to look at its phase diagram first. So, in the left hand side you see here the titanium and nickel in the two extremities of the phase diagram versus temperature.

So, titanium has a quite a high melting temperature of above 1600 °C, nickel also have something like 1460 °C or above and so the around 50-50 composition, the important phase is nickel titanium phase which exhibit the shape memory effect and these nickel titanium phase has a B2 crystal structure. Now, you can have a look that there are many other competing phase along with that nickel titanium phase which has a rather very limited solubility if you decrease the temperature and here almost very less and if you go below 600 °C there is also again a eutectoid decomposition very similar like copper-aluminium system and so we must have to overcome such a situation.

So, the competing phase is here are Ti_3Ni_4 and Ti_2Ni, this is like an enlarge or larger version of this domain, this region, I have enlarged here and the temperature here is shown in Kelvin. So, you can have a look that even though around 1400 K there is a large limit, but ultimately it completely reduces. These are all experimental measured solubility limit curve with nickel content.

So, one has to design the alloy very carefully so that we get the composition and temperature and transformation temperature accurately.

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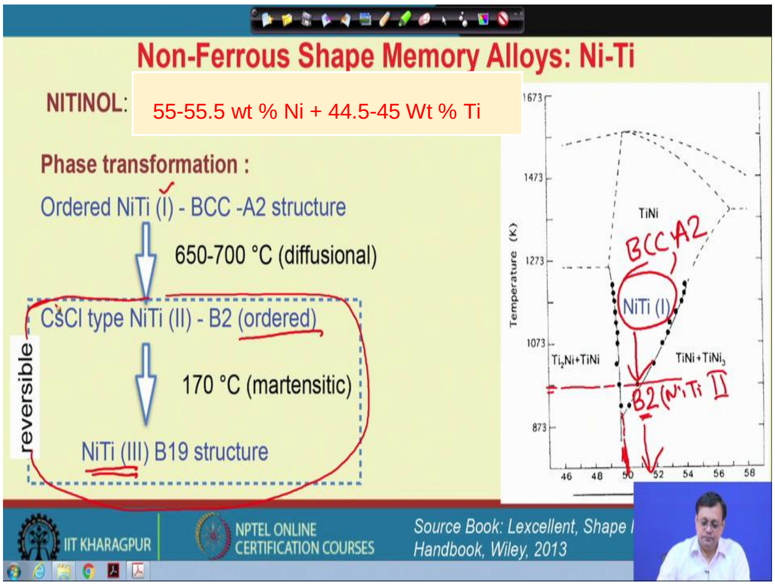

Non-Ferrous Shape Memory Alloys: Ni-Ti

NITINOL: 55-55.5 wt % Ni + 44.5-45 Wt % Ti

Phase transformation :

Ordered NiTi (I) - BCC -A2 structure

650-700 °C (diffusional)

CsCl type NiTi (II) - B2 (ordered)

170 °C (martensitic)

NiTi (III) B19 structure

reversible

Source Book: Lexcellent, Shape
Handbook, Wiley, 2013

So, mostly people preferred that this NITINOL which has been discovered quite a long time ago, it has a very limited composition range and people have exploited the properties of like 44.5 to 45 % of titanium and let say the > 50 % of the rest of the component should be the nickel. So, let us once again have a look at the diagram here, so nickel is a little bit here is the less one and now the phase transformation occurred that has a ordered nickel titanium phase which has a BCC A2 structure. We are talking about the nickel-titanium system at higher temperature, which is shown here and marked here as 1.

So, this has a BCC structure which is a A2 structure and if we cool it down so around 650 to 700 °C there is a diffusional transformation, means if we cool it down to 700 means something around 923 °C, around this temperature range the B2 phase will appear which is an ordered phase, which is known as nickel-titanium here I marked it as 2.

And this B2 phase is the parent phase which transform martensitically to a B19 type of martensite structure and these here it is shown here as NiTi3. So, the shape memory effect that is achieved in this composition range is lying in this particular reversible transformation, because here there is a CsCl type of structure, which is the parent austenite structure that transform martensitically to a B19 structure. And once again if you reheat the B19 structure, it will again be transformed into B2 type of ordered structure. However, once again I should remind you that there are other competing transformations that occur which are not at all desirable in this particular case.

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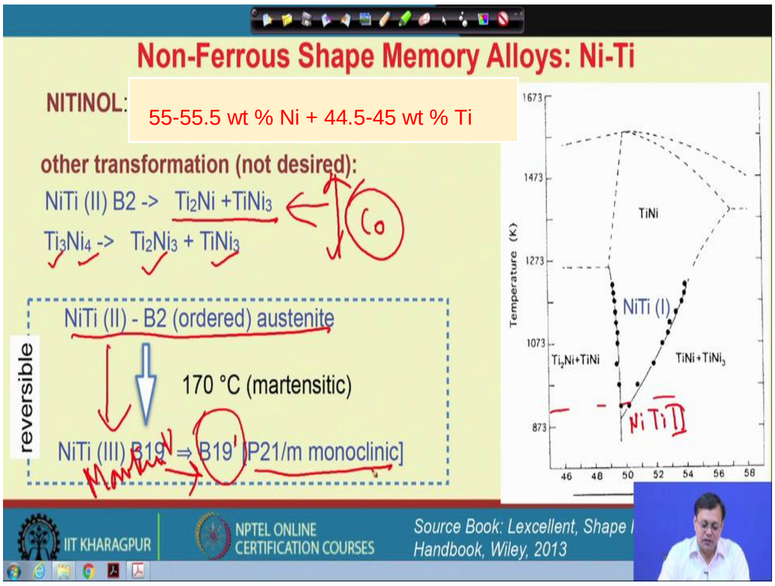

Non-Ferrous Shape Memory Alloys: Ni-Ti

NITINOL: 55-55.5 wt % Ni + 44.5-45 wt % Ti

other transformation (not desired):

NiTi (II) B2 -> $Ti_2Ni + TiNi_3$

Ti_3Ni_4 -> $Ti_2Ni_3 + TiNi_3$

reversible

NiTi (II) - B2 (ordered) austenite

170 °C (martensitic)

NiTi (III) B19 ⇒ B19' [P21/m monoclinic]

Source Book: Lexcellent, Shape … Handbook, Wiley, 2013

Now, in case of this nickel-titanium where NiTi (II) means the ordered structure that produces at a relatively lower temperature then 700 °C, that particular phase will be decomposed into Ti_2Ni and $TiNi_3$ and this is a eutectoid transformation which is not desired at all. There are some other transformation like Ti_3Ni_4 which again further decomposes into Ti_2Ni_3 or $TiNi_3$ type of phase. So, there are so many different transformation occurred and this could be somehow avoided by adding some amount of cobalt into the system which retard those transformation and stabilizes the nickel titanium.

However, once again there are so many different complex transformation that occurred in titanium nickel system, because I said about the B2 structure that transform into B19 type of martensite structure. So, this is the martensite structure; however, in some cases B19' phase form, so here this dash stands for an ordered type of martensite and this martensite has a monoclinic structure with the symmetry of P21 m.

So, this is M stands for actually monoclinic, so this is a monoclinic structure and you could easily realize how difficult this transformations are, because once the austenite is ordered. And martensite is also ordered during reverse transformation all these ordered structure should come back otherwise thermodynamically it is not at all favorable and therefore, we have to look at how these transformation sequence are linked with their.

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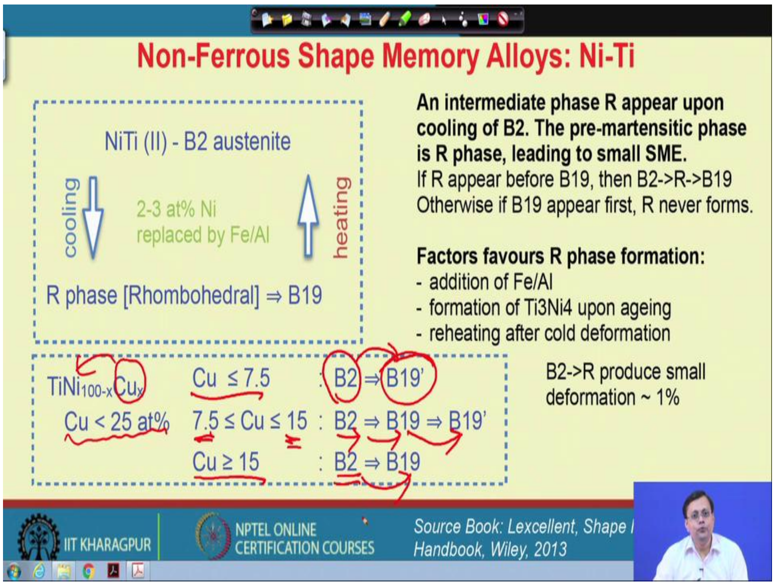

Non-Ferrous Shape Memory Alloys: Ni-Ti

NiTi (II) - B2 austenite

cooling

2-3 at% Ni
replaced by Fe/Al

heating

R phase [Rhombohedral] ⇒ B19

An intermediate phase R appear upon cooling of B2. The pre-martensitic phase is R phase, leading to small SME.
If R appear before B19, then B2->R->B19
Otherwise if B19 appear first, R never forms.

Factors favours R phase formation:
- addition of Fe/Al
- formation of Ti3Ni4 upon ageing
- reheating after cold deformation

$TiNi_{100-x}Cu_x$

$Cu < 25$ at%

$Cu \leq 7.5$: $B2 \Rightarrow B19'$
$7.5 \leq Cu \leq 15$: $B2 \Rightarrow B19 \Rightarrow B19'$
$Cu \geq 15$: $B2 \Rightarrow B19$

B2->R produce small deformation ~ 1%

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Source Book: Lexcellent, Shape
Handbook, Wiley, 2013

So, let us have a look how these B19 or B19' phase forms and whether there are some other phases again formed or not. The austenite phase where the B19' is a common transformation and in some cases it has been observed that before B19 martensite formation, there are competing phase, there is a R phase that forms. Here R basically stands for the a rhombohedral type of structure, means before a B19 martensite, the B2 during cooling transform into R and then this R will transform into B19. And such a particular transformation occur when 2 to 3 at. % of nickel is replaced by some iron and aluminum, so there is such a problem appear; however, there are some benefit of R phase formation.

So, this intermediate phase or R phase that appeared during cooling of this B2 structure is a pre-martensitic phase, we often call it as a pre-martensitic phase and due to such transformation we get a very small shape memory effect, because ultimately we need to deform B19 plastically and then during heating it should go back to B2 phase and that amount is less and therefore, we get very less amount of a shape memory effect.

Now, it has been observed that if R phase that appear before B19 means if such a sequence of transformation occurred then the transformation occur from B2 to R to B19 otherwise. If B19 appear first means during any transformation if B19 has formed then we can simply rule out the formation of the R phase, because R phase will never appeared in the structure or in the microstructure.

So, we can think about why we really need these R phase because, these R phase formation produces very small amount of transformational strain and that is why sometimes it may or may not be preferred. However, we can control these R phase formation because when the alloy contain iron and aluminium these R phase transformation become more favored or sometimes during aging itself if some Ti_3Ni phase type of precipitate appeared in the microstructure, then again this R phase transformation will be promoted.

Or sometimes after cold deformation to reduce the vacancies, we reheat the microstructure, some of the component and during that time also some times the R phase formation is promoted. And this is a very general sequence that the transformation will occur directly from a B2 type of austenite instead of forming directly B19. The transformation goes in this way, first R phase forms and then it goes into B19 type of martensite.

However such a transformation is linked with nickel titanium system only by little addition of iron or aluminium; however, people have a tried with copper to replace this nickel. So here you see I write here like if this is the total 100 % and we add copper purposely in order to replace nickel. However, copper addition never goes beyond 24-25 atomic %, so means like titanium 50 nickel 25 copper 25, that is the maximum composition and people do not prefer more than that, because there will be no other transformation occurring and martensitic transformation will be retarded.

So, in a very low copper content in case let say in the range of 7.5 atomic % of copper this B2 will transform directly to B19', here this an ordered martensite structure. However, in the range of 7.5 to 15, it has been observed that B2 first transform to B19 and then B19 will undergo a ordering that is B19' whereas, in case of higher copper content we may get a direct B2 to B19 type of structure.

So, you can see the sequence of phase transformation in a nickel-titanium system is very complex and there are many different competitive transformation like, eutectoid transformation which I discussed just a few minutes ago, that the eutectoid transformation like here the Ti_2Ni type of phase, Ti_2Ni type of phase or $TiNi_3$ type of phase or let say the Ti_2Ni_3 type of phase or Ti3Ni4 phase. These are competitive phases that evolve with the NiTi phases.

However, even though we preferred a higher amount of nickel content in this composition, but mostly they are in the martensite itself, there are many different variants that appear, like instead of B19 we may get sometime B19' or sometimes we get R phase.. So, there are 3 phase we have learned in a nickel-titanium system and now we will try to move a little bit further and to learn how the path is chosen for such a B19 from B2 parent phase.

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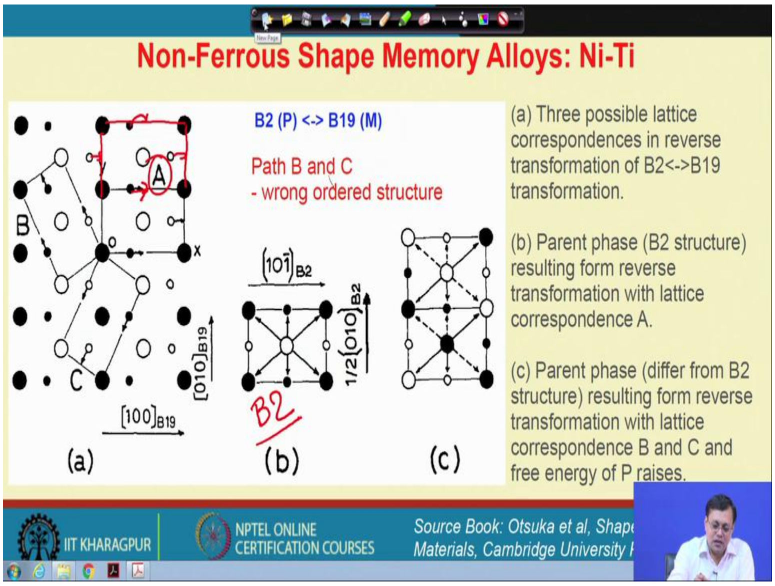

Non-Ferrous Shape Memory Alloys: Ni-Ti

B2 (P) <-> B19 (M)

Path B and C
- wrong ordered structure

(a) Three possible lattice correspondences in reverse transformation of B2<->B19 transformation.

(b) Parent phase (B2 structure) resulting form reverse transformation with lattice correspondence A.

(c) Parent phase (differ from B2 structure) resulting form reverse transformation with lattice correspondence B and C and free energy of P raises.

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

Here a schematic diagram is shown to understand the crystallography in nickel titanium. So, the larger field bubbles represent a particular type of atom which may there are possibility either can be here or here. So, let us say this is a B2 type of structure, first B2 means let us say a ordered type of structure and inside that it is a BCC base structure. So you can get a one type of atoms here and this is a second type of atom is a very general case like how these ordering takes place. So, this is another one type of atom where the possibility of getting this atom can be also here and this is a typical direction of <100> of B19 and this is <010> of B19 martensite.

So, from parent phase we can think about basically three different possible correspondence lattice how, let us say a A type of lattice where this is the structure of the lattice, this atom will should move here and this will move here and this will move here. The second is the B type, so one is the A type, another one is the B type and the third one is the C type. Here you see this is again the same structure and we can get this from the in the martensite B19 structure.

Now, the transformation that is required from B2 to B19, that is a parent phase to a martensite phase is that is a desired phase; however, the three different correspondence that occurred by the reverse transformation from B19 to B2, because once it is an ordered structure we have to go back from a B19 to a B2 structure. Now how is the B2 structure, that is the parent B2 structure, if we take a A type of B19 structure and transform into a B2, then how it will looks like? this. So here at the atoms and this is another one this is the alternative position of this atom and this is another 4 atoms, so this is the ordered structure and it is the 1/2 <010> direction of B2.

So, we basically get back the initial ordered structure to A of the parent structure, so how it is again? you can have a look here. So, if I join this lattice, so I simply move it here, I simply move it here, I simply move it here, I move it here. So it is a A type of lattice and I get back the original B2 structure from a A type of lattice.

And now interestingly if I choose other different correspondence like B and C then from here you could easily see that I will develop such a structure, where the original structure it seems will not be back. Because here this should be in the alternative directions right and here should be the black one and here should be the opposite one. So that will be a problem to get back the original parents structure and the transformation strain will never be back.

So, it is very much important that which way the system choose to transform from a product phase that is martensite to its parent phase, which basically linked with the parent phase it differ from the B2 structure. Because this is not the original parent structure, which is desired, which we have started with, so this is just a wrong sequence actually.

So from a path B and C if we choose any of these lattice correspondence and try to go back to the parent structure which is the B2 instead of going that it basically goes here and so, the free energy of the parent phase basically rises and the transformation is not possible.

So, the reverse transformation from B2 to B19, this reverse transformation and their lattice correspondence is very much important, because there is an ordered structure and if we have to again get back that ordered structured parent phase then a proper lattice correspondence has to be chosen. That is why this is not only a case for nickel titanium for many other system also, wherever there is a B2 to B19 type of structural transformation actually occur.

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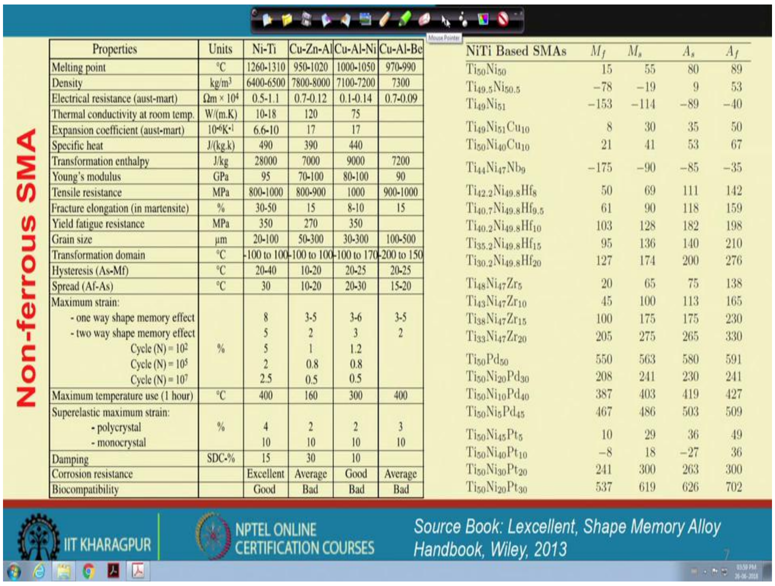

Non-ferrous SMA

Properties	Units	Ni-Ti	Cu-Zn-Al	Cu-Al-Ni	Cu-Al-Be
Melting point	°C	1260-1310	950-1020	1000-1050	970-990
Density	kg/m³	6400-6500	7800-8000	7100-7200	7300
Electrical resistance (aust-mart)	Ωm × 10⁴	0.5-1.1	0.7-0.12	0.1-0.14	0.7-0.09
Thermal conductivity at room temp.	W/(m.K)	10-18	120	75	
Expansion coefficient (aust-mart)	10⁻⁶K⁻¹	6.6-10	17	17	
Specific heat	J/(kg.k)	490	390	440	
Transformation enthalpy	J/kg	28000	7000	9000	7200
Young's modulus	GPa	95	70-100	80-100	90
Tensile resistance	MPa	800-1000	800-900	1000	900-1000
Fracture elongation (in martensite)	%	30-50	15	8-10	15
Yield fatigue resistance	MPa	350	270	350	
Grain size	µm	20-100	50-300	30-300	100-500
Transformation domain	°C	-100 to 100	-100 to 100	-100 to 170	-200 to 150
Hysteresis (As-Mf)	°C	20-40	10-20	20-25	20-25
Spread (Af-As)	°C	30	10-20	20-30	15-20
Maximum strain:	%				
- one way shape memory effect		8	3-5	3-6	3-5
- two way shape memory effect		5	2	3	2
Cycle (N) = 10^2		5	1	1.2	
Cycle (N) = 10^5		2	0.8	0.8	
Cycle (N) = 10^7		2.5	0.5	0.5	
Maximum temperature use (1 hour)	°C	400	160	300	400
Superelastic maximum strain:	%				
- polycrystal		4	2	2	3
- monocrystal		10	10	10	10
Damping	SDC-%	15	30	10	
Corrosion resistance		Excellent	Average	Good	Average
Biocompatibility		Good	Bad	Bad	Bad

NiTi Based SMAs	M_f	M_s	A_s	A_f
$Ti_{50}Ni_{50}$	15	55	80	89
$Ti_{49.5}Ni_{50.5}$	−78	−19	9	53
$Ti_{49}Ni_{51}$	−153	−114	−89	−40
$Ti_{49}Ni_{51}Cu_{10}$	8	30	35	50
$Ti_{50}Ni_{40}Cu_{10}$	21	41	53	67
$Ti_{44}Ni_{47}Nb_9$	−175	−90	−85	−35
$Ti_{42.2}Ni_{49.8}Hf_8$	50	69	111	142
$Ti_{40.7}Ni_{49.8}Hf_{9.5}$	61	90	118	159
$Ti_{40.2}Ni_{49.8}Hf_{10}$	103	128	182	198
$Ti_{35.2}Ni_{49.8}Hf_{15}$	95	136	140	210
$Ti_{30.2}Ni_{49.8}Hf_{20}$	127	174	200	276
$Ti_{48}Ni_{47}Zr_5$	20	65	75	138
$Ti_{43}Ni_{47}Zr_{10}$	45	100	113	165
$Ti_{38}Ni_{47}Zr_{15}$	100	175	175	230
$Ti_{33}Ni_{47}Zr_{20}$	205	275	265	330
$Ti_{50}Pd_{50}$	550	563	580	591
$Ti_{50}Ni_{20}Pd_{30}$	208	241	230	241
$Ti_{50}Ni_{10}Pd_{40}$	387	403	419	427
$Ti_{50}Ni_5Pd_{45}$	467	486	503	509
$Ti_{50}Ni_{45}Pt_5$	10	29	36	49
$Ti_{50}Ni_{40}Pt_{10}$	−8	18	−27	36
$Ti_{50}Ni_{30}Pt_{20}$	241	300	263	300
$Ti_{50}Ni_{20}Pt_{30}$	537	619	626	702

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

Now, let us have a look at what are the various system so far we have discussed, so in case of a copper-nickel and copper, copper-zinc system we have added aluminium and these are some of the properties of these systems, please have a look in case of a melting temperature, density.

So something very much interesting to notice here like a copper-zinc, copper-aluminium, a copper-aluminium beryllium system the melting temperatures are relatively lower than the nickel-titanium. So here nickel-titanium is preferred for in such a case whereas, if you simply look at the biocompatibility the nickel-titanium is the best as a biocompatible elements.

and the beryllium containing alloy is not preferred at all; however, if we look about the one way or two way shape memory effect then the maximum strain can be generated in a nickel-titanium system which is around 8 % which is huge strain actually. So we can get back that strain whereas, the transformation domain is very well in case of a copper-aluminium-beryllium system where we can go from -200 to almost 150, so we can tune the transformation temperature a large.

And so this is for a very industrial application we can have a very useful and if you look about the tensile strength they are somewhat in the range of 800 to 1000 MPa. So, which is quite good and also we may have a relatively low young's modulus that can be achieved in this case where the total transformational enthalpy is very high in case of nickel-titanium.

The expansion coefficient is also very less in case of nickel-titanium and so there is a large biomedical application by looking at these properties of nickel-titanium we can simply suggest. So, that is very good in case of such a system whereas, in case of a high temperature behaviour the copper-aluminium-beryllium system could be exploited more. Now, in case of this nickel-titanium system, there are so many different alloy composition I have shown, here these are somewhat a nickel-rich alloy so you can see the nickel 50 or 0.5 or 51.

So, in this particular case the M_f or M_s temperature could be tuned from a 55 to -114 in Ni-Ti system. so that is why we said that the transformation domain could be -100 to +100. So this is quite good, but not so good compared to copper-aluminium-beryllium system. Whereas, if you replace nickel with the help of some amount of copper then we can think about getting a much lowered M_s and niobium, hafnium, zirconium, palladium or platinum these are some of the elements that can replace some of these composition and so that we can tune the martensitic transformation temperatures quite wide.

So, let us say in case of titanium-palladium system we can reach up to 550 °C whereas, we can also go up to - 175 °C. So you can see there is a large possibilities of all these different shape memory alloys and there are application oriented material development that goes on during this period. And if we critically look at some of these titanium-nickel system, then you will see that here I show here x, which is the atomic % of a ternary alloy addition in nickel-titanium system with the change of M_s temperature that is represented with ΔM_s.

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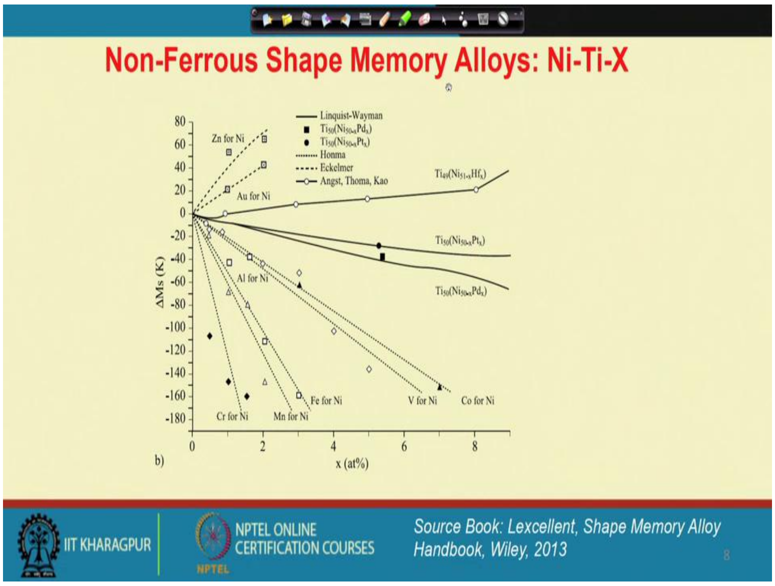

Non-Ferrous Shape Memory Alloys: Ni-Ti-X

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

So, I am just talking about the change, so if we first take an example like gold or let us say the palladium. So, usually the hafnium concentration if we increases then M_s temperature goes in the positive side where chromium for nickel or manganese for nickel, they change the transformation temperature quite a lot like cobalt or let us say in case of palladium, we can change the M_s to a negative side to a to a large extent.

So, far we have discussed the most important systems or non-ferrous systems in non-ferrous shape memory alloy and we have learnt that, various transformational product that may encountered during these austenite to martensitic transformation and the situation could be very complex in case of nickel-titanium. So the purity of the alloy is also important. Why we are discussing about that? Because sometimes we may producing some alloy from not a very let us say the highly pure elemental composition let us say 1 % or 0.1 % aluminium is there in a nickel-titanium alloy which will change the all the transformation temperature.

So, the purity of this advanced alloys or shape memory alloys are very much important, so that for a particular type of application we know the selected M_s and M_f temperatures. And with this we complete today’s discussion on the non-ferrous shape memory alloy and we will continue some other case studies and particular mechanical properties and the application oriented discussion in the next classes.

Thank you.