University Of Technology- Iraq
Department of Materials Engineering
General Materials Branch
Fourth class

Smart Materials

Lecture 3 : Types of Shape Memory Alloys

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Types of Shape Memory Alloys

1. Gold Based Shape Memory Alloys
2. Ni-Ti Shape Memory Alloys
3. Copper Based Shape Memory Alloys
4. Fe-Based Shape Memory Alloys
5. Other Types of Shape Memory Alloys

Gold Based Shape Memory Alloys

- The first SMA ever discovered was an Au-47.5%Cd alloy. Olander used electrochemical techniques to identify its B2 cubic (austenite) and B19 orthorhombic (martensite) phases.
- In 1975, the South African Chamber of Mines sponsored a major research effort on gold-based SMA. In detail, the interest was focused on a combination of gold-zinc and copper-zinc memory alloys,19 leading to some patents. The nominal compositions of the investigated compounds varied between 60 and 40% for the gold and 15 and 30% for the copper, while zinc was usually taken by difference.known as the Heusler alloy(Au-30%Cu-10%Zn)

Gold Based Shape Memory Alloys

- In these alloys, shape-memory properties show in a wide range of compositions, allowing then a certain flexibility in the composition to optimize workability, mechanical strength, and ductility at room temperature where strain recovery gets values up to 6%. Because of the high cost it did not take off

Gold Based Shape Memory Alloys

- Gold alloys are considered for applications where their typical color and their characteristic corrosion and tarnish resistance are important. The excellent electrical conductivity of gold makes them particularly suitable for use as electrical connectors,
- Their most natural use is in the jewelry industry, for instance, for manufacturing mounts.
- Other uses can be found in dentistry. Because of the strong thermoelectrical coupling, gold-palladium (Au-Pd) alloys find applications in thermal measurements.

Application of Gold Based Shape Memory Alloys

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MAGNETIC SHAPE MEMORY ALLOYS(MSMA)

- The magnetic shape memory alloys (MSMAs) or ferromagnetic shape memory alloys are smart materials that exhibit large strain under application of an external magnetic field. Typical MSMA materials are:
- FePd, CoNiGa, $LaSrCuO_4$, FePt, CuAlNi, and the most studied NiMnGa
- The phenomenon of magnetostriction, where an external magnetic field can change the dimensions of the sample, was observed already in 1842 by Joule.

What is the deference between Magnetostrictive materials and MSMAs

- In normal ferromagnets, such as Fe or Ni, the strains associated with the magnetostriction are of the order of 1-4%, whereas materials with exceptionally large magnetostriction, for example Tb-Dy-Fe alloys (Terfenol-D), show strains of the order of0.1%.
- In contrast, MSMAs differ from other Magnetostrictive materials, such as Terfenol-D and Galfenol, as they produce much larger strains up to 10%, under relatively low bias magnetic fields
- The mechanism is based on the magnetic anisotropy of the material. In fact, the MSMA effect differs from ordinary magnetostriction not only for the strains of two orders of magnitude larger, but also for a different mechanism.
- Although ordinary magnetostriction is observed in structurally homogeneous samples, the MSMA effect requires a special microstructure that is provided by a martensitic transformation

- In general, each region has twins with different orientation because of the magnetization during the material manufacturing. By applying an external magnetic field, two phenomenas can occur:
- 1. The magnetic moments can rotate without macroscopic phenomenology.

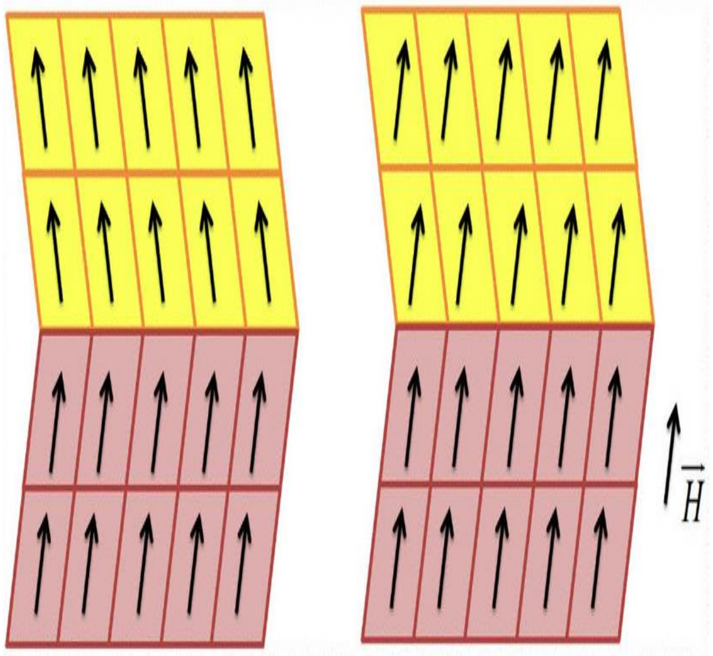
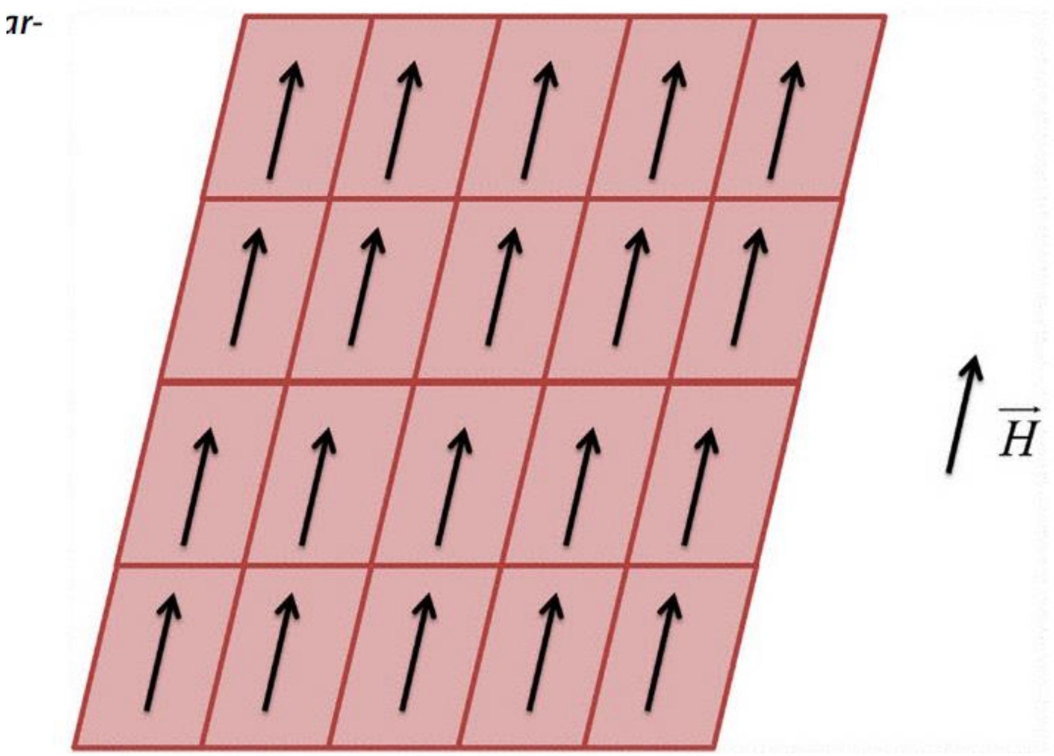


Figure 2.13 *Magnetic Moments without the External Field.*

2. There is the MSMA effect; hence, the twins orient themselves along the direction of the external field, providing large shape changes



the basic requirements for the appearance of the MSMA effect are:

1. The material should be (ferro)magnetic and exhibit a martensitic transformation.
2. The magnetic anisotropy energy must be higher than the energy required to move a twin boundary

MAGNETIC SHAPE MEMORY ALLOYS

Table 2.3 MSMA Properties

Maximum Linear Deformation	100,000 με
Available work ($\sigma \cdot \varepsilon$)	300 MPa · 1000 με
Young modulus	7.7 GPa
Average resistivity	80 μΩ cm
Curie temperature	From 320 to 380 K
Martensitic transition temperature	From 160 to 620 K
Change of martensitic transition temperature as composition change of 1%	50 K

MSMA, magnetic shape memory alloys.

Cu –Based Shape Memory Alloys

- The centered cubic intermetallic phase β of binary alloys Cu-Zn and Cu-Al exhibits a martensitic transformation, but the transformation temperatures that can be obtained by varying the composition are extremely low (practically lower than 50°C for Cu-Zn) or too high (over 100°C for Cu-Al).
- The addition of a third element (Al for Cu-Zn, Ni or Be for Cu-Al) enables us to obtain martensitic transformations,
- The temperatures for which can be adjusted by the composition, over a wide range.

Cu –Based Shape Memory Alloys

- As can be seen in Phase diagrams, the β phase is only stable above temperatures of around 500°C. Given that for these alloys, the shape-memory effect can only take place below 200°C, it is necessary to perform quenching from the domain of stability of the β phase. Quenching will enable us to obtain an alloy with a β phase that is metastable at the transformation temperature.
- In the case of copper-based shape-memory alloys (and the same is true for NiTi-based alloys), it is enough that the quenching process be sufficiently quick to prevent diffusion reactions. In certain cases, even air-quenching may suffice (e.g. in the case of Cu-Zn-Al (8% weight) alloys).

Cu –Based Shape Memory Alloys

There are Three Major Copper Based Shape Memory Alloys

1. Cu-Zn-Al Shape Memory Alloy
2. Cu-Al-Ni- Shape Memory Alloy
3. Cu-Al-Be Shape Memory Alloy

Copper-Zinc-Aluminum SMA

- Cu-Zn-Al is a ternary compound commercially relevant and widely studied in bibliography. Zinc was selected because of its low cost and wide availability on the market. This alloy presents transformation temperatures in the range between - 100 and 100 C, a function of both the composition and the thermomechanical treatments.
- Historically, Cu-Zn-Al was the first copper-based SMA to be commercially exploited.
- Typical compositions are 15-30% Zn, 3-7% Al, and Cu to add to 100%.

Copper-Zinc-Aluminum SMA

- Cu-Zn-Al alloys exhibit excellent properties of shape memory and pseudo-elasticity. It is possible to adjust the transformation temperatures within a very extensive range, between 0°C and over 150°C. It is relatively easy to shape these alloys.
- Yet the main problem with them means that they are not widely used for industrial applications and that they are not stable above or around 130°C.
- Beyond this temperature, the β phase, which is not at thermodynamic equilibrium, has a tendency to decompose, which leads firstly to a decrease in the transformation temperatures and then very quickly to the disappearance of the shape-memory effect properties.
- Hence, these alloys can only be used for applications where the temperature will never go above a hundred degrees centigrade.

Copper-Zinc-Aluminum SMA

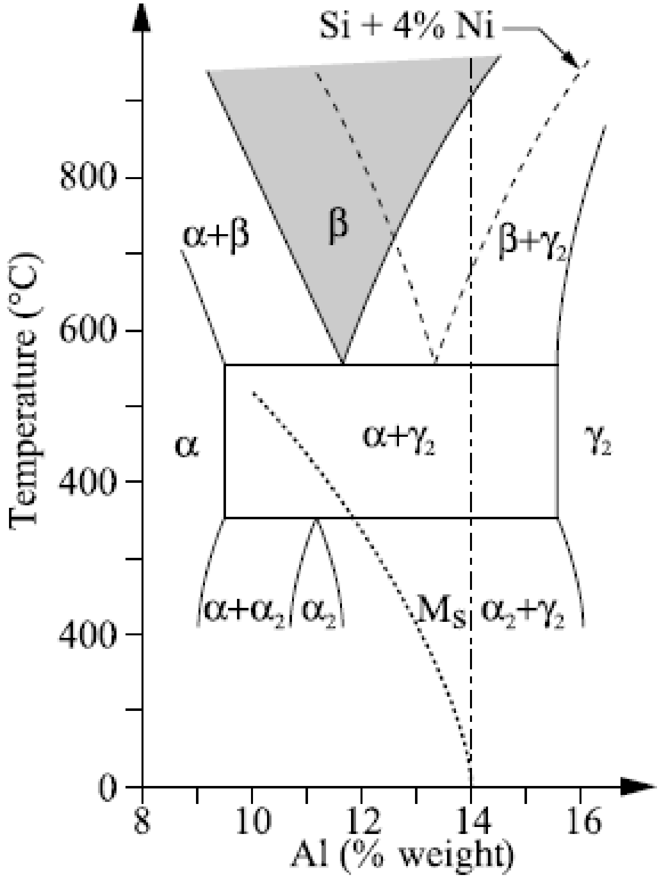
- The major advantage of the Cu-Zn-Al alloys is the cost, being made of relatively inexpensive metals and produced through conventional processes such induction melting (requiring small quantities of additives like zirconium or titanium, to reduce grain size) or powder metallurgy.
- Their memory properties are significant, with a maximum recover-able strain of about 5%. Cold workability is feasible and results a strong function of the Al percentage. Additive quantities must be kept low, because they can affect the internal stability of the chemical structure and then, the shape memory characteristics. Cu-Zn-Al alloys may exhibit two-way shape recovery mechanism, depending on the training process.

Copper-Aluminum-Nickel SMA

- Nickel is adopted as a valid alternative to zinc, and cheap as well. Cu-Al-Ni has undergone extensive development and is usually preferred among the copper alloys. A typical composition is made of 13% Al, 4% Ni, and Cu to balance.
- Transformation temperatures are in the range between 80 and 200 ^{o}C. As with the former compound, it is cheap and may be processed by standard methods.
- The mechanical characteristics may be improved by using the same additives already mentioned for Cu-Zn-Al.
- Furthermore, small per- centages of Mn (replacing equal quantities of Al) reduce the transformation temperatures. Again, extra elements can affect the stability of the alloy and therefore their use must be limited.

Copper-Aluminum-Nickel SMA

- As we saw above, the β phase of the Cu-Al diagram also exhibits thermoelastic martensitic transformation. Figure .shows the equilibrium diagram for Cu-Al (solid
- The addition of nickel causes a shift in the domain of stability of the β phase in relation to the transformation temperature curve without noticeably changing the rest of the diagram.
- the corresponding alloy (with around 14% Al) is very brittle.
- In practical terms, we can only use alloys with lower aluminum concentrations, with a martensite start temperature of around 200°C.



Cu-Al-Be Shape Memory Alloys

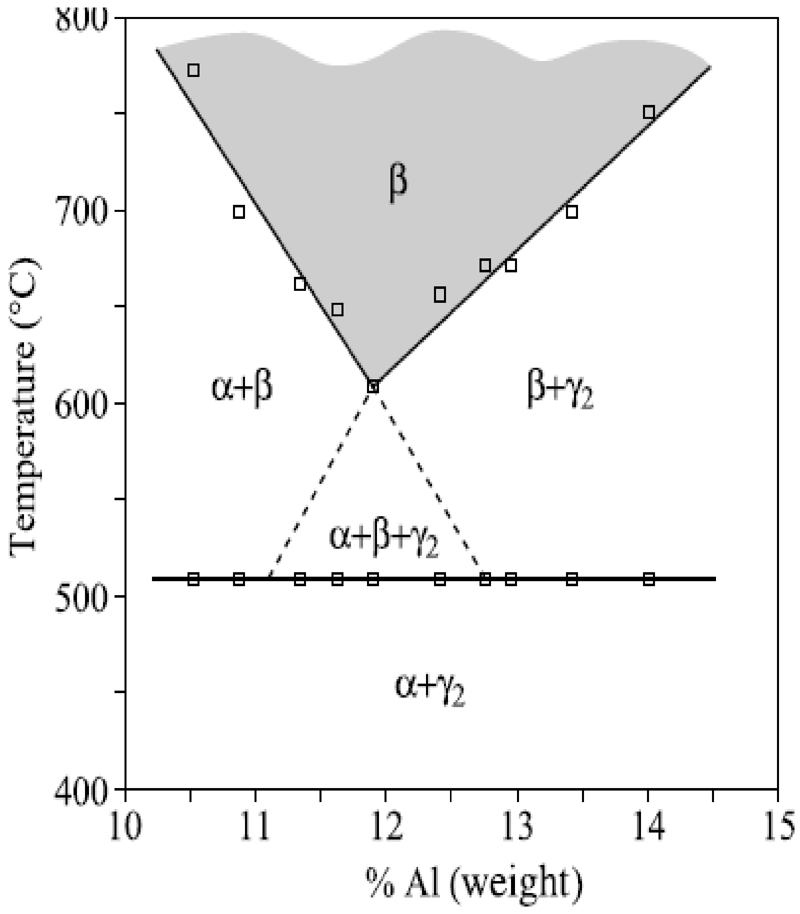
- Another alloy, obtained by replacing Ni with Be, has achieved some commercial acceptance. It is more expensive, but small percentages of Be (0.5%) allows extending
- the transformation temperature range to an interval between- 200 and 100 C. Besides, it shows excellent super-elastic and damping properties.

Cu-Al-Be Shape Memory Alloys

- The addition of beryllium in a small proportion modifies the equilibrium diagram for Cu-Al: the temperature of the eutectoid plateau is reduced, and above all the curve of the transformation temperatures is brought down.
- The martensite formed is 9R. Unlike the effect of nickel, beryllium in a low concentration does not affect the composition or the temperature of the TTT (time-temperature-transformation) diagram. Figure 2.6 shows part of the phase diagram for Cu-Al-Be (vertical cross-section at 0.47%wt beryllium.

Cu-Al-Be Shape Memory Alloys

- this Figure shows the influence of the beryllium and aluminum content on the M_s temperature



Cu-Al-Be Shape Memory Alloys

- For industrial use, Cu-Al-Be presents the cumulated advantages of Cu-Zn-Al and Cu-Al-Ni: the possibility to adjust the transformation temperatures between a very low temperature and 200°C by altering the concentrations of the elements in the alloys, and excellent heat resistance, up to 200°C.
- However,

1. similarly as for Cu-Al-Ni, the samples can only be shaped at high temperatures, around 600°C.
2. Another disadvantage of this alloy is the presence of beryllium, as beryllium oxides are very dangerous in terms of health. Even so, the beryllium is present only in very small amounts and in an alloy-bound form. The only precaution that needs to be taken with

- this alloy is not to overheat the samples, mainly during the manufacturing process.

Cu –Based Shape Memory Alloys

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/m^3	6400-6500	7800-8000	7100-7200	7300
Electrical resistance (aust-mart)	$\Omega m \times 10^4$	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)	$10^{-6}K^{-1}$	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

IRON-BASED SHAPE MEMORY ALLOYS

- Ferrous-based compounds have been developed as an alternative to Ni-Ti alloys and to Cu-based compositions due to their low cost and good properties. Fe-SMA were discovered and developed in Japan
- in the basic Fe-Mn-Si version. The alloying elements Cr, Ni, and Co were subsequently added to improve shape recovery properties. Fe-Mn-Si-Cr-Ni-Co alloys show several other attractive features, making them suitable for various technological applications.
- More recently, addition of small amounts of Va or Nb have been also investigated.104 Again, grain size has a specific importance in the overall properties of the alloys.

IRON-BASED ALLOYS

- Fe-SMA are produced by combinations of hot rolling, cold rolling, forging, drawing, and others. With respect to Ni-Ti alloys, the shape memory effect in these materials is far smaller, 4% at most, and generally occurs at higher temperatures.
- Since Fe-based SMA are mostly used as joints, recovery stress is more important than recovery strain. In fact, in this case the most important property is the maximum force exerted by the SMA element, after warming and constraining it to the reference structural components

Ni-Ti Shape Memory Alloys

1. Ni-Ti Shape Memory Alloy
2. Ni-Ti-X Shape Memory Alloy (X = Pd, Pt, Hf or Zr)
3. Porous Ni-Ti Shape Memory Alloy
4. Ni-Ti-Cu Shape Memory Alloy

Ni-Ti SMAs

- The maximum Ms transformation temperature that can be obtained with this alloy is around 70°C.
- Figure shows that a slight increase in the N content of the alloy causes a decrease in th temperature.
- Below 50% nickel, the Ms temperature is independent of the composition and remair at its maximum value.
- This is very easy to understand in view of the equilibrium diagram which shows that for these sub-stoichiometric oncentrations, the alloys are in the bi-phase domain Ti_2Ni β, with a concentration of the β

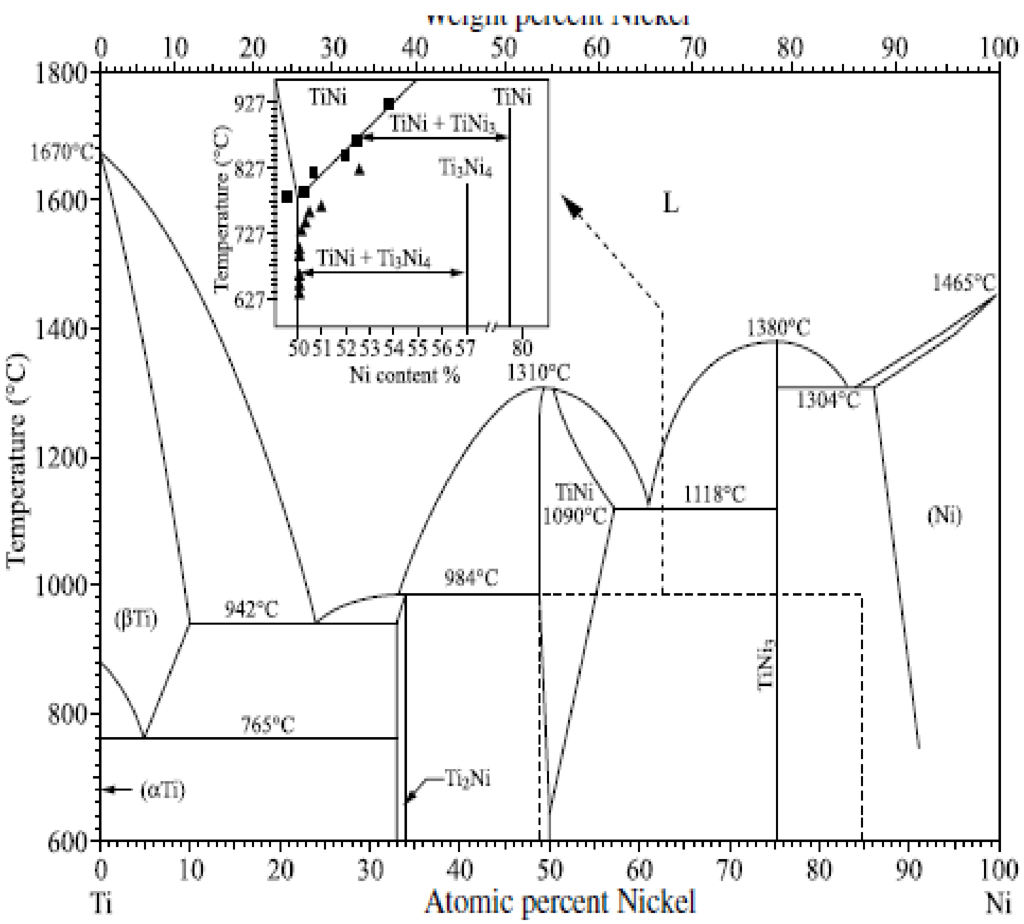


Figure 2.9. *Equilibrium diagram of Ti-Ni*

Ni-Ti SMAs

- if the martensitic transformation occurs first, we do not observe the R phase. It is very uncommon, when the substance is heated, to observe the reverse transformation M => R => β. The factors which favor the existence of the R phase are:

1. the substitution of a few percent of nickel by iron or aluminum;
2. the formation of precipitates Ti_3Ni_4 by aging of Ti-Ni with a high nickel content;
3. reheating after cold deformation.

POROUS Ni-Ti

- Over the last decades, porous Ni-Ti has attracted great interest because it is characterized by SE and good mechanical properties, good corrosion resistance, and biocompatibility.
- Porous Ni-Tis have been introduced after a few years by the discovery of unusual shaped memory properties of dense Ni-Ti alloys
- Porous NiTi combine the main shape memory characteristics of SMA with benefits common to other porous or foamed metals, such as low density, high surface area, and high permeability

POROUS Ni-Ti

- The properties and the phase transition temperatures of porous NiTi alloy depend on the foam microstructure and on the different NiTi phases that can form during the manufacturing.
- Further, anisotropy, nonuniform pore distribution and irregular pore shape can determine poor mechanical properties of porous NiTi SMAs
- biomedical applications are the main target for porous NiTi that represents one of the most promising materials for orthopedic implants.
- In fact, it allows ingrowth of osteoblasts and tissues, promoting long-term fixation of bone implants, and is characterized by lower Young’s modulus and pseudoelastic behavior similar to hard tissues like bone and tendons

POROUS Ni-Ti

- However, before clinical application, some issues need to be resolved,
- for example, release of nickel into surrounding tissue because of corrosion of NiTi in the biological environment and wear debris released from implants at the interface with bio- logical tissues.
- Ni release may induce adverse symptoms, ***as allergic response, cytotoxicity, and genotoxicity leading to serious health problems.***
- To reduce Ni release, ***many surface treatments have been developed able to create uniform and thick TiO_2 films on NiTi surfaces.***

Ni-Ti-X SMA (X = Pd, Pt, Hf or Zr)

- Numerous elements have been tested to increase the transformation temperatures of Ti-Ni .
- Unfortunately, nearly all the elements tested actually decrease the transformation temperatures.
- The only elements which increase these temperatures are gold, hafnium, platinum and palladium, but even then, only with high concentrations of them (except in the case of gold).
- The price of these elements is prohibitive for their extensive use.

Ni-Ti-Cu Shape Memory Alloy

- At present, the most commonly used element in an alloy with Ti-Ni is copper, substituting for some of the nickel.
- The effect of copper is to decrease the hysteresis and the spread of the martensitic transformation without having too great an effect on the values of the transformation temperatures.
- In addition, copper inhibits the formation of the R phase
- It is this alloy which is most often used in applications, except in surgery and medicine for reasons of problems of biocompatibility

NiTi Based SMAs	M_f	M_s	A_s	A_f	Reference
$Ti_{50}Ni_{50}$	15	55	80	89	[49]
$Ti_{49.5}Ni_{50.5}$	−78	−19	9	53	[56]
$Ti_{49}Ni_{51}$	−153	−114	−89	−40	[4]
$Ti_{49}Ni_{51}Cu_{10}$	8	30	35	50	[56]
$Ti_{50}Ni_{40}Cu_{10}$	21	41	53	67	[56]
$Ti_{44}Ni_{47}Nb_9$	−175	−90	−85	−35	[45]
$Ti_{42.2}Ni_{49.8}Hf_8$	50	69	111	142	[57]
$Ti_{40.7}Ni_{49.8}Hf_{9.5}$	61	90	118	159	[57]
$Ti_{40.2}Ni_{49.8}Hf_{10}$	103	128	182	198	[57]
$Ti_{35.2}Ni_{49.8}Hf_{15}$	95	136	140	210	[57]
$Ti_{30.2}Ni_{49.8}Hf_{20}$	127	174	200	276	[57]
$Ti_{48}Ni_{47}Zr_5$	20	65	75	138	[58]
$Ti_{43}Ni_{47}Zr_{10}$	45	100	113	165	[58]
$Ti_{38}Ni_{47}Zr_{15}$	100	175	175	230	[58]
$Ti_{33}Ni_{47}Zr_{20}$	205	275	265	330	[58]
$Ti_{50}Pd_{50}$	550	563	580	591	[49]
$Ti_{50}Ni_{20}Pd_{30}$	208	241	230	241	[49]
$Ti_{50}Ni_{10}Pd_{40}$	387	403	419	427	[49]
$Ti_{50}Ni_5Pd_{45}$	467	486	503	509	[49]
$Ti_{50}Ni_{45}Pt_5$	10	29	36	49	[49]
$Ti_{50}Ni_{40}Pt_{10}$	−8	18	−27	36	[49]
$Ti_{50}Ni_{30}Pt_{20}$	241	300	263	300	[49]
$Ti_{50}Ni_{20}Pt_{30}$	537	619	626	702	[49]

Applications of Shape Memory Alloys

Alloy	Main Applications
Au-based	Dental
	Jewelry
Ni–Ti	Pipe couplings
	Electrical connectors
	Actuators
	Orthodontics
	Stents
	Surgery implants
Cu-based	Seismic attenuation
	Isolators and dampers in civil constructions
	Reinforcing elements
	Connectors and couplings
	Safety valves and other safety devices
Fe-based	Tube couplings
	Rail couplings
	Seismic attenuation

Main SMAs

Table 2.1 Main SMAs

Alloy	Composition	Transition Temperatures, °C	Hysteresis, °C
Ag-Cd	44/49 wt% Cd	[−190,−50]	15
Au-Cd	46,5/50 wt% Cd	[30,100]	15
Cu-Al-Ni	14/14,5 wt% al, 3/4,5 wt% Ni	[−140,100]	35
Cu-Sn	15 wt% Sn	[−120,30]	10
Cu-Zn	38,5/41,5 wt% Zn	[−180,−10]	10
Cu-Zn-x (X = si, Sn, al)	few wt% of X	[−180, 200]	10
In-ti	18/23 wt% Ti	[60,100]	4
Ni-Al	36/38 wt% al	[−180,100]	10
NiTi	49/57 wt% Ni	[−50,110]	30
Fe-Pt	Approx. 25 wt% Pt	Around −130	40

SMA, shape memory alloys.

Comparison between NiTi, CuZnAl, and CuAlNi Alloys

Table 2.2 Comparison between NiTi, CuZnAl, and CuAlNi Alloys

Property	NiTi	CuZnAl	CuAlNi
Maximum temperature shape recovery	100 °C	120 °C	200 °C
Maximum recoverable strain	8%	6%	5%
Hysteresis	12–50 °C	10–25 °C	15–20 °C
Austenite yield stress (MPa)	415	350	400
Martensite yield stress (MPa)	70	80	130
Break stress (MPa)	700	600	500–800
Density (g/cm^3)	6.05	7.6–8.0	7.02
Resistivity (μΩ cm)	80–90	8.5–9.7	11–13
Thermal capacity (J/(Kg K))	837	400	373–574

Workability of SMA Alloys

Type	Forming	Cold Working	Machinability	Transformation (°C)
Au-based	Good	Poor to very poor	Fair to good	−50 to 100
Ni–Ti	Poor to very poor	Fair to poor	Poor	−100 to 100
Cu-based	Very good to good	Poor	Good	−200 to 200
Fe-based	Very good to good	Good to poor	Fair to good	−200 to 150