A comparative review of the (Potential) Shape Memory Alloys.

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Introduction

The shape memory effect is not a phenomenon occuring in a very limited amount of alloys and compositions. The effect has been observed not only in systems exhibiting a thermoelastic but also in those showing a non-thermoelastic martensitic transformation, a quasi-martensitic transformation and even a second order transitions.
When it comes to the point of applying those alloys in an industrial context, only a few systems remain attractive, mainly because of the price/quality ratio. Nevertheless, a continuous effort is going on to improve the physical and mechanical properties of these alloys, to extent the boudary conditions for applications, such as temperature, strain, force, amount of cycles to other limits and of course to reduce the cost-price by improving and shortening the way of processing finished products.
In this lecture, we will therefore review the three most important systems, Ni-Ti, Cu-based and Fe-based alloys. We will compare their properties which are specifically of interest but also the direction, each system is being developed to fulfil more severe conditions for applications.
For each system, we will discuss the most appropriate composition, the data related to the shape memory effect and related to the mechanical behaviour. Finally, the way in which further development occurs will be pointed out.

The Cu-based alloys

The Cu-Zn and the Cu-Al system form the basis of all technical Cu-based SMB alloys. The important compositon range is the one in which these alloys show a stable β-Hume-Rothery phase. This composition domain widens at higher temperatures. The β-phase can transform into a martensitic phase if cooled below the M_s-temperature. The M_s-temperature is strongly composition dependent and may occur at temperatures where the β-phase is no longer thermodynamically stable. In this conditions, the material has to be solution-treated followed by a quenching procedure in order to avoid the decompositon of the beta-phase into lower energy phases such as the α and γ-phase. At relatively low temperatures the beta-phase will behave metastable and only further slow cooling may be required to transform martensitically.
Figure 1 and figure 2 show the phase-diagrams of the Cu-Zn and Cu-Al system.
The reasons for developing at least ternary alloys are the following :

1. The β-Cu-Zn alloys show martensitic transformtions only at low to very low temperatures (0 K - 270 K).
2. the β-Cu-Al alloys have very high transformation temperatures (500 K - 750 K) but the beta and martensite will decompose very fast above 600 K.
3. Adding a third element that changes the M_s-temperature creates one degree of freedom more in adjusting the composition to the required M_s-temperature. Figure 3 for example shows the straight lines of constant M_s in a ternary Cu-Zn-Al diagram.

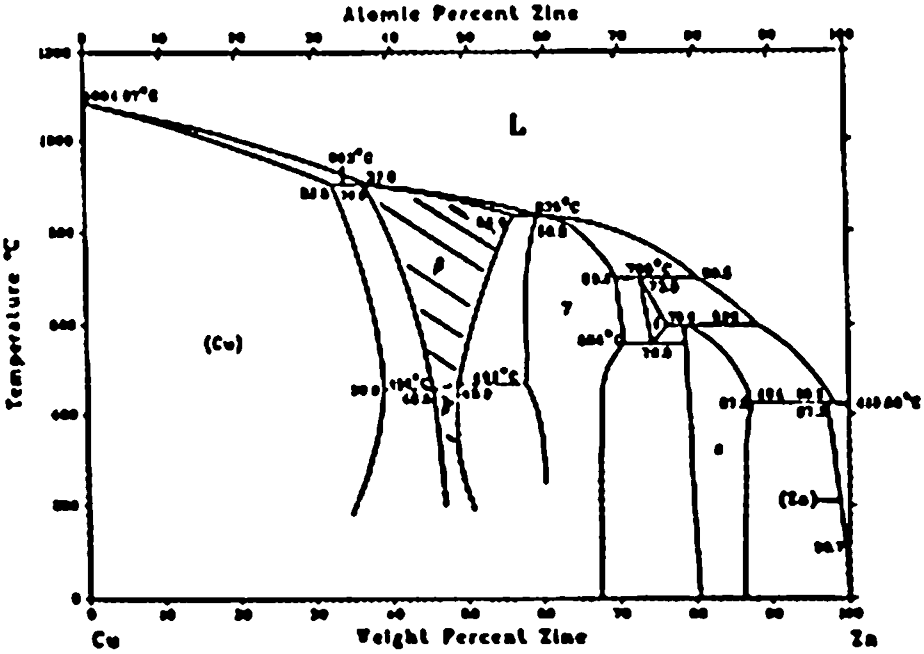


Figure 1 : Cu-Zn phase diagram

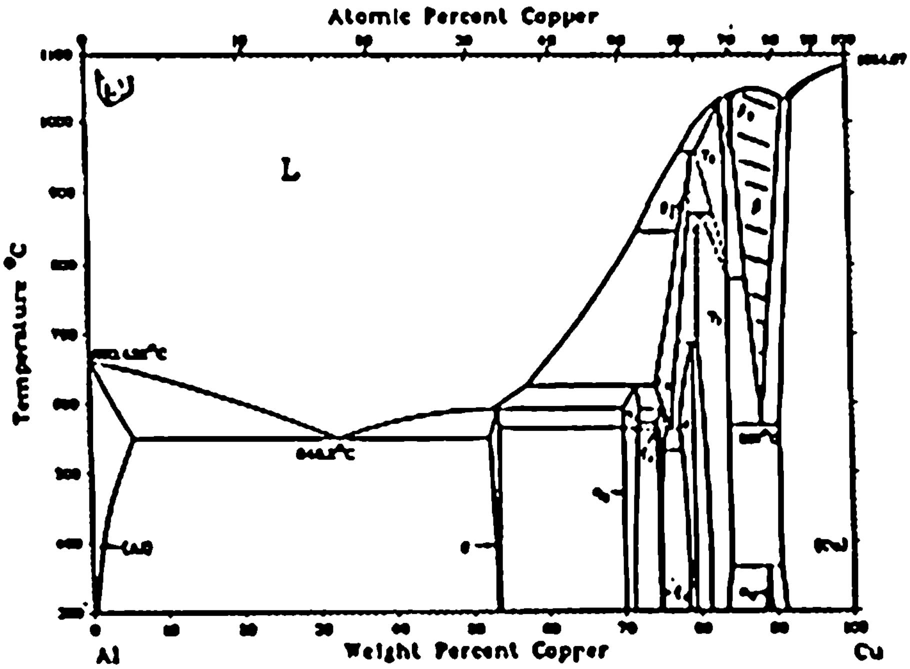


Figure 2 : Cu-Al diagram

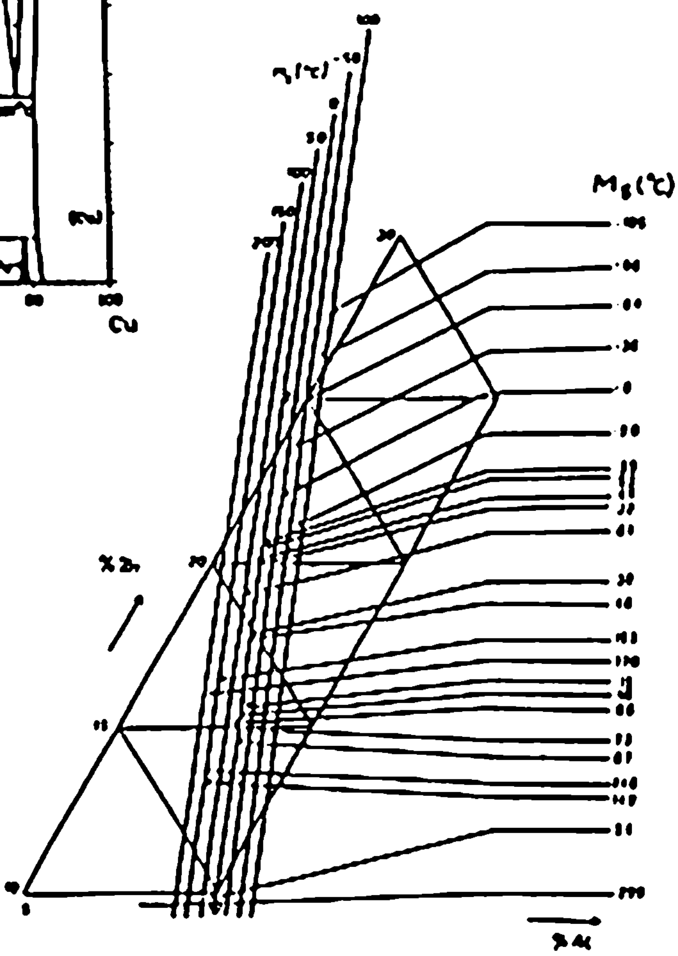


Figure 3 : lines of constant M_s-values in the Cu-Zn-Al diagram

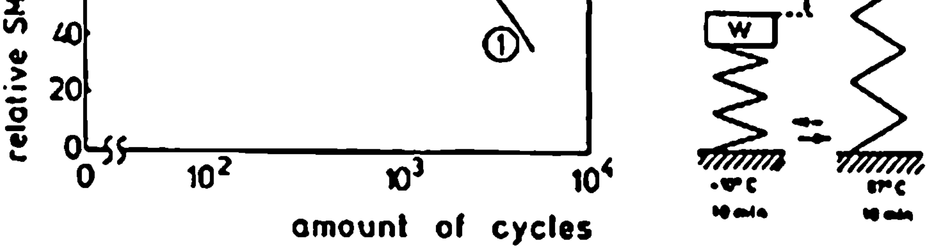
The compostion range of Cu-based alloys

From the Hume-Rothery rules it is known that the β-phase is most stable for an electron to atom ratio e/a = 1.48. The higher the temperature in the β-phase field the more e/a of the β-alloy can deviate in both ways from this ideal value. Lower values of e/a will promote first the formation of the ductile α-phase during cooling while higher values of e/a will promote the formation of the very brittle γ_2-phase.
For phase-stability reasons, discussed later, the choice however is limited and is different for the two most important families of the Cu-based alloys : Cu-Zn-Al and Cu-Al-Ni
The compositions of Cu-Zn-Al have generally a value of e/a ≤ 1.48. since all M_s-values between almost absolute zero-temperature and 100°C can be obtained. Alloys with higher M_s are very prone to decomposition.
As already mentionned, smaller e/a-values will promote α-formation. If a sufficient α-volume fraction can be obtained, cold-processing, especially wire-drawing becomes possible which is more convenient and economic than hot working.
But the lower the value of e/a the higher the driving force for α-formation. This requires higher quenching rates to retain the full β-condition at low temperatures. An other reason to approach e/a = 1.48, is that stabilisation, as explained later, is less pronounced in alloys with higher e/a-values.
To conclude, the most stable alloys are obtained for e/a = 1.48. but lower values can offer better opportunities for processing. Therefore, the composition of Cu-Zn-Al is classified in three groups : 4% Al, 5% Al and 6% Al. Generally lower % Al allows better and easier machining while an Al-content higher than 6% Al makes the alloys harder and difficult to proces.
Cu-Al-Ni alloys are more stable at higher temperatures and the M_s-temperatures have an upper limit of about 180°C. Lower values can be obtained by increasing the Al-content since the Ni is only added between 3 and 5 wt% and reduces the M_s only by 15 to 20 degrees per wt%. The Al-content is situated between 12 and 14 wt%. For those reasons, e/a is always > 1.48. and the precipitation of γ_2-phase prior to α-phase cannot be suppressed.
As a consequence, Cu-Al-Ni alloys cannot be cold worked and are generally also very brittle. Since they have some important advantages relative to Cu-Zn-Al alloys, mainly the higher transformation temperature and the absence of martensite stabilisation, the elaboration of those alloys has received a lot of interests with very succesful results as will be explained later.

The shape memory characteristics

The martensitic transformation occurs thermoelastically and the M_d-temperature is about 100°C above M_s. The high structural anisotropy of the material makes that the uniaxial full-recoverable shape deformation varies between 10% (<001> - direction) and 3% (<111 > - direction). In fine grained polycrystalline material a one-way shape recovery of almost 6% is possible but the two-way effect is limited to 4%. The maximum stress recovery of a shape memory element is of the order of 700 MPa.
The shape memory effect may be limited by the following items (1) :
a. the hysteresis of the martensitic transformation
b. overheating in the beta-phase
c. stabilisation of the martensitic phase
d. shape memory degradation
The hysteresis is generally rather small, 5 to 20 degrees in polycrystalline material. For most on/off applications this effect is not of importance as the A_s-temperature is in these cases the most important parameter.

However, the hysteresis limits the development of controlling or steering shape memory devices since inversing the temperature rate postpones temporary the shape memory action. Another important aspect, observed during partial transformation, is the so-called transformation creep. When one cycles between two temperatures well within the transformation zone the forward and reverse shape changes of trained material during respectively cooling and heating are not equal so that a (small) drift may occur as a function of cycles. This drift is annihilated after a full transformation cycle.
The Cu-based materials are limited in upper temperature. Since β is metastable it will decompose into its equilibrium phases α and γ or bainite, another non-equilibrium phase. For those reasons, the upper temperature to which a shape memory element can be exposed, is taken as the temperature at which the material can remain during maximum one hour without any significant damage to its properties. For Cu-Zn-Al alloys this temperature is of the order of 200°C while for Cu-Al-Ni 300°C is the maximum allowed temperature during one hour.
Stabilisation of the martensite is so far only significantly observed in Cu-Zn-Al alloys and is an effect of ageing of the martensitic phase. The most important effect is the increase of the reverse transformation temperatures, A_s and A_f. This limits the use of these alloys in devices that should react at a critical temperature even after a long time at lower temperature. The degree of stabilisation is of the order of a few degrees per year up to more then 20 degrees per year dependent on the material composition and the ageing temperatures. Lower e/a - values, thus lower Al-content, and higher temperatures enhance the stabilisation. Moreover, stabilisation can increase dramatically and even prevent normal reverse transformation and thus also the memory effect, if no proper heat-treatment has been given to the material. This heat-treatment should be so that the beta-phase contains its equilibrium vacancy-concentration prior to transform to martensite. This can be realised either by slow cooling or step-quenching the alloys. Step-quenching is quenching above the M_s temperature and storing the material sufficiently long time in order to obtain the equilibrium vacancy-concentration.
Since Cu-Al-Ni alloys are not prone to stabilisation these alloys can be quenched immediately to below the M_s temperature. However, such fast quenching creates a low degree of DO_3 ordering of the β-lattice which depresses the transformation temperatures.
Ageing in the range 200°C - 300°C restores the ordered state rather fast and will increase the reverse transformation temperatures. In order to obtain stable transformation temperatures it is therefore recommanded to age the specimens for about 30 minutes at 300°C after quenching.
The most important instability is the degradation of the shape memory effect . Figure 4 gives an example of this phenomenon. Degradation is an effect that



	①	②	③
Diameter of the wire (mm)	2	2	3
Diameter of the spring (mm)	13	13	14
Amount of coils	6	7	5
Initial displacement (mm)	20	20	15

Figure 4 : degradation of a SME-spring

accelerates during cycling and is dependent on several factors : the higher the required shape recovery, the higher the relative degradation and the broader the temperature range in which cycling occurs, the slower the degradation. Also, the higher the dynamic and/or static load, the faster degradation will occur.
It is thought that degradation is due to plastic accomodation during the martensitic transformation and stabilisation of particular shape memory variants. Therefore in sequence of increasing sensivitivity to degradation the Cu-based SME alloys can be classified as Cu-Al-Ni and Cu-Zn-Al alloys.

The mechanical properties

Unalloyed ternary Cu-based beta alloys show generally a very large grain size in the order of mm, which limit the fracture strain of martensite and beta at low temperatures to a few percent.
The problem has been solved by adding other elements in order to create precipitates that limit the grain size and grain growth. The most promissing additions are Zr(0.4wt% to 1.2wt%), Co(0.4wt% to 0.8wt%), Ti(0.5wt% to 1wt%) and B(0.4wt% to 0.2wt%). It has been observed that Zr, Co and B are most effective in Cu-Zn-Al alloys, while Ti is most effective in Cu-Al-Ni alloys. An average grain size of 50µm - 100µm is now steadily obtained and the fracture strain in martensite is of the order of 10%, which is sufficient for shape memory applications.

Recent developments in Cu-based alloys

As previously mentioned Cu-Al-Ni alloys are very difficult to process and have generally high transformation temperatures. At the other side, the system is not prone to stabilisation. In order to improve the ductility of these alloys Mn can be added, replacing partially the Al-content. Mn is a betastabilising element with an e/a ratio equal to 1. This makes that heat-treatment can occur at low betatising temperatures which might reduce the quenching rates. Also α-phase can be obtained because e/a is now ≤ 1.48. Since also lower transformation temperatures can be obtained it is thought that the Cu-Al-Ni-Mn-Ti alloys could be an unique Cu-based system covering a very broad temperature range of transformation temperatures (-50°C to +180°C) with excellent shape memory characteristics.
Especially progress in stabilisation and degradation is expected. The composition range of these alloys is not yet optimised, but will be of the following order :
Al(8wt%-13wt%)-Mn(2wt%-5wt%)-Ni(2wt%-5wt%)-Ti(0.5wt%-1wt%)-Cu(balance).

The Ti-Ni alloys

Ni-Ti is the eldest and best explored system of all shape memory alloys, though many new results are recently presented especially related to the R-phase and the influence of alloying third elements. Although those alloys show certainly the best shape memory behaviour, they have some important desadvantages relative to the Cu-based alloys : they are much more expensive and are very difficult to melt and to elaborate. However, their excellent corrosion resistance and stable configuration make them, for example, the only SME alloys suitable for implantation in human bodies.

The composition of Ni-Ti alloys

Ni-Ti is an intermetallic phase composition that has some solubility at higher temperatures (figure 5). The compositions of the Ni-Ti-SME alloys are approximately between 48 and 52 at %Ni and the transformation temperatures are very sensitive to the nickel-content (a decrease of about 150 degrees for an increase of 1 at %Ni).
The transformation temperatures can be choosen between -40°C and +100°C. The addition of third elements increase also here the degree of freedom and decrease the sensitivity of the transformation temperatures to the composition. However, so far no really successful alloying for these purposes has been reported yet. Alloying elements have been added for other purposes too. The addition of a few % Fe, for example, separates the R-transition in Ni-Ti further from the martensitic transformation, while the addition of small amounts of Nb offer the possibility to postpone the reverse transformation and thus the shape memory effect to much higher temperatures. The transformation temperatures are recovered after the first heating.(2)
A very recent development is the replacement of Ni by Pd (order of 20%).(3). This creates alloys with high transformation temperatures (200°C - 300°C).
It is clear that these alloys will be used only if no other technique is available to solve the problem and so far no unique use or mass availability of these alloys have been reported.

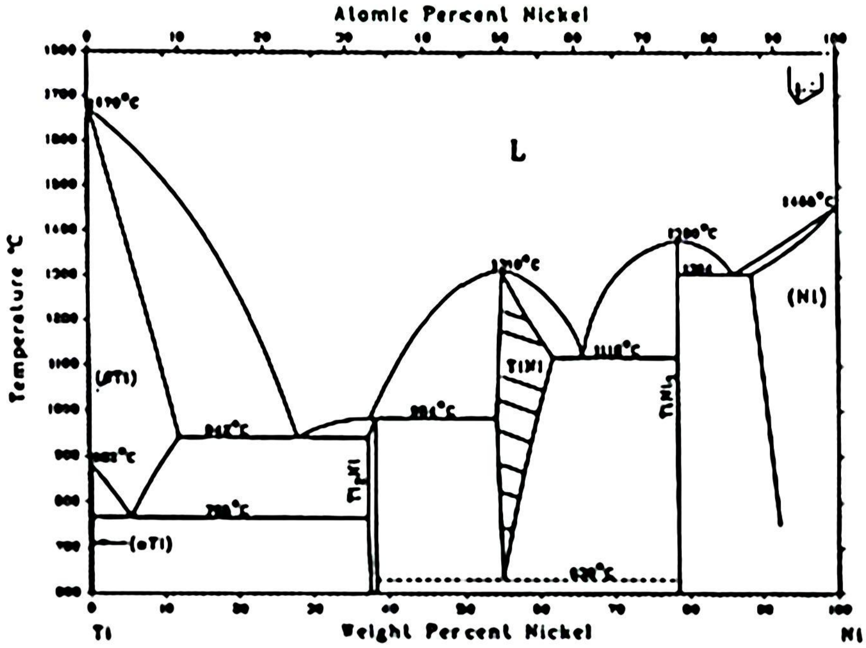


Figure 5 : Ni-Ti phase diagram

The shape memory behaviour

Ni-Ti alloys show the best shape memory behaviour of all SME alloys. Even in polycrystalline state 8% shape recovery is possible and even 8% pseudo-elastic strain is completely reversible above A_f, while the recovery stress is of the order of 600 MPa.
To obtain this result, the material has to be cold-worked in the last production step, followed by proper heat-treatment.
But the Ni-Ti alloys are also prone to some "instabilities". The hysteresis of the martensitic transformation is higher than the one of Cu-based alloys

(about 2 times) and the transformation temperatures shift to other values due to thermal cycling. This shift can be either positive or negative dependent on the previous heat-treating temperature and prestrain given prior to the treatment and can be in the order of 10 degrees.(4)
Although degradation is also observed, it is certainly less pronounced than in Cu-based alloys. In case an order of 10^6 cycles is required the maximum two-way memory effect should be also limited to less than 0.5%.
A lot of attention has been given in recent years to the R-phase-transition. The R-transition is a B2 = rombohedral transformation that has also second-order characteristics (5) and always preceeds the martensitic transformation without being a real premartensitic phenomenon.
The most specific characteristics of this R-phase transition is that is shows a clear one- or two-way memory effect in order of magnitude of 1% recoverable strain and that the hysteresis of the transformation is very small, only a few degrees.(figure 6) This can offer special possibilities for accurately regulating devices.
Many reports related to this R-phase exists but only few systematic works has been presented.(6, 7, 8, 9) It has been shown that the appearance of the R-phase can depend on the alloying elements such as Fe(10) but also in Ni-Ti it can appear dependent on the heat-treatment and the compositions. At the same time the transformation temperature is changing, dependent on the heat-treatment temperature and the applied stress as schematically illustrated in figure 7 (6).
It can be mentioned here that the R-phase plays an important role in the so-called All-Round Shape Memory Effect (11), a special kind of shape memory effect, that will be not treated here.

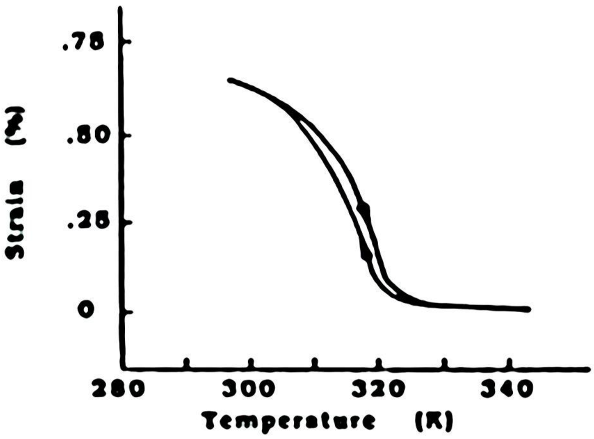


Figure 6 : shape memory effect related to the B2 $\rightleftarrows$ R transition in Ni-Ti (σ = 200 MPa)

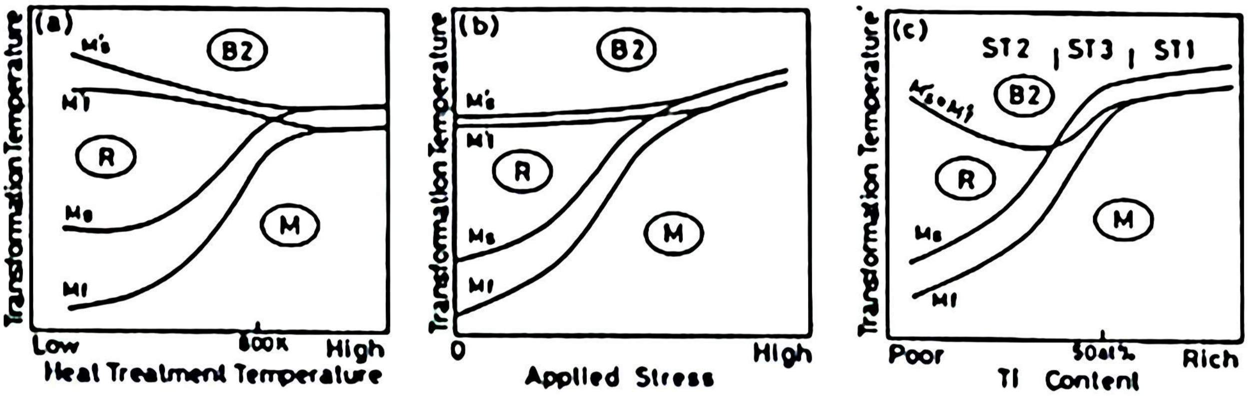


Figure 7 : schematic illustration of the effect of (a) heat treatment after cold work, (b) applied stress and (c) composition on the transformation in Ni-Ti alloys

Mechanical properties

Ti-Ni alloys have a grain size in the order of a few µm. They are very ductile, even cold, and deformation strains of 60% to 70% are possible. The small grain size permits also to draw wires to only some tenths of a millimetre without creating a bamboo-structure.
The high work-hardening however, makes these alloys very difficult to machine, to cut or to saw so that intermediate heat-treatment during processing is required.

The Fe-Mn-Si alloys

Several Fe-based alloys, with thermoelastic or non-thermoelastic transformation, show a more or less significant shape memory effect. An excellent review of these alloys is given by Maki et al.(12)
Presently a large amount of interest has been given, especially to the Fe-Mn-Si alloys because they have a rather large hysteresis (the martensitic transformation is non-thermoelastic). The reverse transformation temperatures are around 150°C while the forward transformation temperatures are at, or below, roomtemperature and a one-way shape memory effect of about 5% (13) is possible. These properties make these alloys very attractive for coupling-applications.

The composition range of Fe-Mn-Si alloys

Figure 8 (14) summarizes in a condensed but clear way the interesting composition range and the influence of other alloying elements.
The critical parameter in these alloys is the position of the Néel temperature of the austenite relative to the M_s temperature. To obtain a good shape memory it is necessary to control the M_s as well as the Néel temperature. Indeed, the anti-ferromagnetic ordering of the gamma-phase stabilises the austenite so that martensite will not transform spontaneously. If T_N lies high above M_s, even stress-induced transformation does not take place. Mainly the Mn affects the martensite and magnetic phase transformation temperatures. M_s decreases as Mn content increases, while the Néel temperature increases.
The composition should be so adjusted that $T_N \leq M_s$.

The shape memory characteristics

Since the martensitic phase has been formed non-thermoelastically, reorientation of the martensitic variants will not occur. Therefore, the cold shape has to be formed by deformation above the M_s temperatures during which the martensite will be strain induced. It is generally necessary to give prior thermomechanical treatment to the γ-phase in order to increase the yield strength of the parent-phase exceeding the stress that induces the martensite. This is explained more extensively in another lecture at this conference (13). As is shown in this paper a one-way shape memory effect of 5% can be obtained. A significant two-way effect has not been elaborated yet. Another problem in this system is that $A_s \leq M_s \leq A_f$. This signifies that pseudo-elasticity cannot occur, but more important is that little is known about the value and the stability of the stress recovery during constraint heating. In this respect further research is needed.

Mechanical properties

Since Fe-Mn-Si are austenitic steels, they have very good mechanical properties but the shaping is rather laborious. Heat-treatments should be given in protected atmosphere since these alloys are very sensitive to oxidation, especially at high temperature.

PATENT

KOKAI No.: 62-112720 (5/23/87)

Application No.: 60-249957 (11/9/85)

Inventors: M. Murakami, S. Matsuda, H. Ohtsuka

Applicant: Nippon Steel Corp.

Title: Method of improving properties of Fe-Mn-Si-based SMA

Description:

(1) Iron-based alloy containing 20--40wt% of Mn and 3.5--8wt% of Si is given 20% or less working, and heating to 400°C or above at least once.

(2) Iron-based alloy containing 20--40wt% of Mn, 3.5--8wt% of Si plus 1 or more components from 10wt% or less of Cr, Ni, Co, 2wt% or less of Mo, or 1% or less of C, Al, Cu is given 20% or less working and heating to 400°C or above at least once.

(3) Iron-based alloy containing 20--40wt% of Mn, 3.5--8wt% of Si plus 1 or more components from 10wt% or less of Cr, Ni, Co, 2wt% or less of Mo, or 1% or less of C, Al, Cu, with a further addition of 0.01% or less of Ca or a rare earth element is given 20% or less working and heating to 400°C or above at least once.

- To improve shape memory capability.
- With less than 20% Mn, epsilon-phase as well as alpha'-phase is generated through stress inducement and lowers SME. At above 40%, gamma is stabilized and gamma slip takes priority over gamma-epsilon transformation.
- Si promotes gamma-epsilon transformation at above 3.5%. At above 8%, workability and moldability are impaired.
- Cr facilitates gamma-epsilon transformation and improves shape memory properties as well as corrosion resistance but creates low melt point intermetallic compound with Si at over 10% so that the alloy cannot be melted.
- Ni contributes to strength without impairing shape memory properties but impairs hot workability at over 10%.
- Co improves SME and hot workability but is expensive.
- Mo improves SME and heat resistance but impairs hot workability and shape memory properties at over 2%.
- C improves SME but strength deteriorates dramatically with over 1%.
- Al is used as a deoxidant and improves SME but has no added effect at over 1%.
- Cu improves corrosion resistance without impairing SME but 1% is adequate.
- Ca improves SME through MnS shape control but excessive addition impairs strength and fatigue properties.
- Rare earth elements improves SME through MnS shape control but excessive amounts impair strength and fatigue properties.
- Desirable to keep S and P to 0.003% or less in order to make MnS shape control effect reliable.

Figure 8 : influence of alloying elements on the Fe-Mn-Si alloys properties of shape memory

Conclusion

The choice of a shape memory alloy for applications is much dependent in how far different systems may overlap concerning properties and prices. Especially the later item, price-setting is very difficult. Regardless of this factor, it should be admitted that Ni-Ti alloys are excellent for applications between roomtemperature and 80°C. Beyond these limits Cu-based alloys are certainly the best ones. Generally Cu-based are for all applications the cheapest if these alloys can fulfil the requirements.
Figure 9 gives a full comparison of the three systems : Cu-Zn-Al, Cu-Al-Ni and Ni-Ti. This table should be updated by Cu-Al-Ni-Mn and Fe-Mn-Si or even other systems, but too much data are missing yet.

ITEM	DIMENSIONS	Ni-Ti	Cu-Zn-Al	Cu-Al-Ni
Melting point	°C	1240-1310	950-1020	1000-1050
Density	kg/m^3	6400-6500	7800-8000	7100-7200
Specific Electrical resistance	$10^{-6}\Omega m$	0.5-1.10	0.07-0.12	0.1-0.14
Thermal conductivity (room temperature)	W/m°C	(10-)18	120 (bij 20°C)	75
Thermal dilation coefficient	$10^{-6}.°C^{-1}$	10 (Aust.) 6.6 (Mart.)	16-18 (Mart.)	16-18 (Mart.)
Specific heat	$J\ (kg°C)^{-1}$	470(-620)	390	(400-)480
Thermo-electric power	$10^{-6}\ V.°C^{-1}$	9-13 (mart.) 5- 8 (aust.)	- -	- -
Transformation heat	J/kg	3200	7000-9000	7000-9000
E-modulus	GPa	98	70-100	80-100
Yield-strength	MPa	150-300 (Mart.) 200-800 (Aust.)	150-300	150-300
Tensile strength (mart.)	MPa	800-1100	700-800	1000-1200
Fracture strain (mart.)	% strain	40-50	10-15	8-10
Fatigue limit	MPa	350	270	350
Grain size	10^{-6} m	1-10	50-100	25-60
Transformation temperatures	°C	-50 tot +100°C	-200° tot +120°C	-200° tot +170°C
Hysteresis (A_s-A_f)	°C	30	10-20	20-30
Max. one-way shape memory	% strain	8	5	6
Max. two-way shape memory	% strain			
$N = 10^2$		6	1	1.2
$N = 10^5$		2	0.8	0.8
$N = 10^7$		0.5	0.5	0.5
Super heating temperature (1 h)	°C	400	160-200	300
Specific Damping Capacity	SDC-%	15	30	10
Max. pseudoelastic strain-single crystal	% strain	10	10	10
- polycrystal	% strain	4	2	2

Figure 9 : comparison between Cu-based and Ni-Ti alloys

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