

## CONSIDERATION ON SOME SHAPE MEMORY ALLOYS FROM Cu-Zn-Al AND Ni-Ti SYSTEMS AND THEIR APPLICATIONS

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**Abstract.** In the paper are shown some wide hysteresis shape memory alloys from Cu-Zn-Al system and Ni-Ti based alloys and their applications starting from increasing the hysteresis of the alloys or more precisely by separating austenite start temperature ( $A_s$ ) from martensite start temperature ( $M_s$ ) as far as it is possible.

**Keywords:** shape memory, alloys, hysteresis, applications

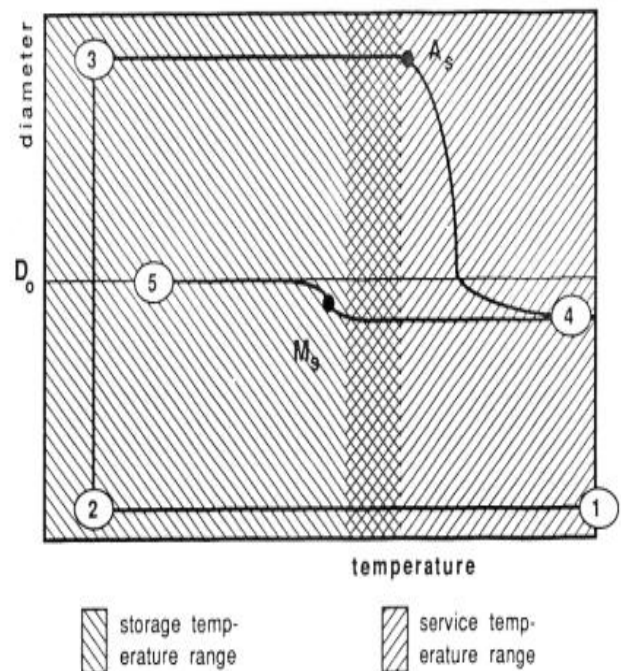
### 1. INTRODUCTION

The first commercial applications of shape memory (and the most successful to date) are as pipe couplings and mechanical fasteners, where shape memory offers advantages in installation time, reliability, weight and versatility. But in order to maintain the integrity of a shape memory joint, be it mechanical or hermetic, it is essential that the installed parts remain austenitic throughout their service life. If they become martensitic, the recovery stresses will be reduced at least to the martensitic yield stress, and more likely, the two-way effect will cause them to decay completely to zero. In the past, this has mandated the use of cryogenic alloys which remain austenitic at all normal service temperature, but must be expanded, stored, inventoried and assembled in liquid nitrogen to prevent premature recovery. Although many users of these products do not consider cryogenics to be a drawback, there is no question that the widespread commercial use of constrained recovery devices will only occur through the elimination of cryogenics.

All solutions to this problem involve increasing the hysteresis of the alloys – or more precisely, separating  $A_s$  from  $M_s$  as far as possible. The reasoning is that  $M_s$  controls the stress decay process mentioned above, while  $A_s$  dictates the maximum storage temperature. This principle is shown in Figure 1.

The alloy is cooled to below  $M_s$  (1-2), the diameter is expanded so that it is larger than that of the tubes ( $D_0$ ) to be joined (2-3), and is then heated until it recovers to make contact with and subsequently crush the tube (4). If subsequent cooling takes place below  $M_s$ , the tube opens up and loses integrity (5). Thus the service temperature range bounded by  $M_s$  and the storage temperature range limited by  $A_s$  (above which premature recovery would make the part useless).

The extent to which the hysteresis must be expanded depends, of course, upon the application. Shipping temperatures can reach 45°C in extreme cases, so the unstressed  $A_s$  of a successful wide hysteresis alloy must be at least that. How low  $M_s$  must be, however, is rather complex since the installed part is under stress and  $M_s$  is a strong function of applied stress.



**Figure 1.** A schematic graph describing how a coupling is made, [1].

In general, one can calculate this from the following equation:

$$M_s < T_s - \sigma_r (\frac{d\sigma}{dT})^{-1} \quad (1)$$

where  $T_s$  is the lowest expected service temperature,  $d\sigma/dT$  is the stress rate of the alloy (typically 5 MPa/°C), and  $\sigma_r$  is the minimum recovery stress needed to maintain product integrity. For commercial couplings that are likely to carry only water and therefore cannot freeze, it may be sufficient to have an  $M_s$  temperature of -40°C; in military applications, where systems must be proofed at -55°C, the zero-stress  $M_s$  must clearly be below -90°C.

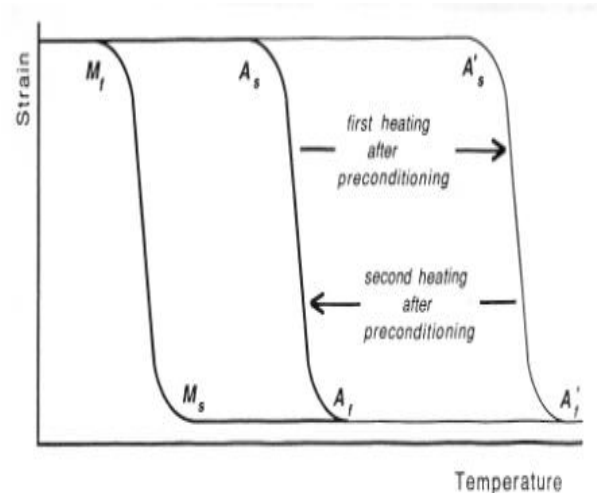
Although there are shape memory alloys which show large hysteresis loops ( $\beta$ -Ti, [1], and iron based alloys,

[2], for example) the strains and recovery stresses of these alloys are insufficient to allow one to design an effective device.  $A_s$  is essentially the same as  $M_s$  in Cu-Zn-Al and exceeds  $M_s$  by only 20 degrees in Ni-Ti, [3]. In order to provide what has been dubbed heat-to-shrink capabilities in these alloys, the hysteresis loops must be significantly expanded from their natural widths. In fact practical methods to expand the hysteresis have been found in both systems. The mechanisms of the hysteresis expansion are quite different in the two cases, but there are similarities in that it is  $A_s$  that is shifted to higher temperatures while  $M_s$  remains unaffected. Both approaches will be individually treated and then compared.

## 2. EXPERIMENTAL

The first alloy to be used in the above described heat-to-shrink mode was Cu-Zn-Al alloy with substantial additions of manganese (roughly 5.0 wt.%) and a greater than normal aluminum concentration (10.0 wt.%). The high aluminum content was chosen to increase the austenite strength, retard stress relaxation at elevated temperature, and improve stress corrosion resistance. The manganese addition was included to shift the eutectoid composition to higher aluminum levels, effectively preventing the formation of the brittle  $\gamma_2$  phase, [3]. The further addition of grain refining agents and adjustments in Zn concentration to tune the  $M_s$  to  $-40^\circ\text{C}$  led to the so-called “Bet alloy” composition which has been in continuous use in constrained recovery applications for over 15 years.

Although the recoverable strain in this alloy is somewhat low (~3%), the alloy is capable of generating high recovery stresses (>400 MPa), is more resistant to stress relaxation than conventional Cu-Zn-Al (with extended service capabilities up to  $125^\circ\text{C}$ ), is of relatively low cost and most importantly, can be produced with a large hysteresis, [2]. The process by which the hysteresis is expanded is called preconditioning and takes advantage of the martensite stabilization phenomenon. When the material is aged in the martensitic phase, that phase is stabilized and the reversion to austenite delayed to higher temperatures – in other words,  $M_s$  remains that of the unaged alloy, while  $A_s$  is increased. The shifted  $A_s$  value is often referred to as  $A_s'$ . It is important to note, however, that the martensite stabilization, or shifting of  $A_s$ , is temporary; once reversion is complete,  $A_s'$  shifts back to the original  $A_s$ . Figure 2 summarized this preconditioning process.

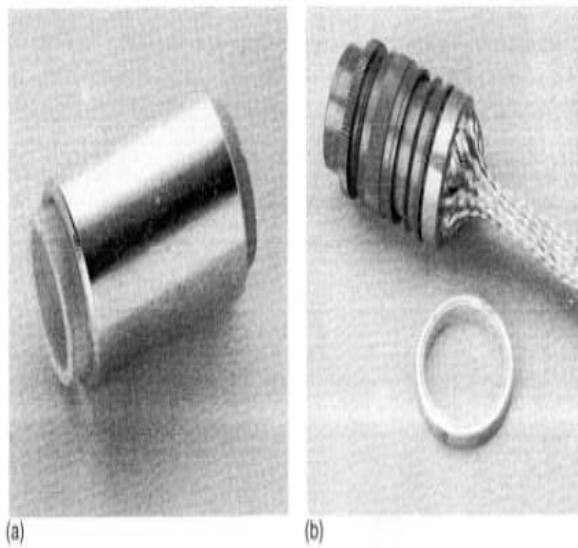


**Figure 2. The preconditioning process is a one-time displacement of  $A_s$  and  $A_f$ . Once recovery is complete, martensite can be reformed, after which  $A_s$  and  $A_f$  are restored to their original values.**

There are three approaches to practical preconditioning:

1. Isothermal preconditioning has already been described: one simply quenches to martensite and holds until  $A_s'$  is shifted to the desired  $45^\circ\text{C}$ . Unfortunately, the activation energy for the aging process is such that this can require several weeks below the  $-40^\circ\text{C}$   $M_s$  of the alloy and thus the process is largely impractical.
2. Non-isothermal preconditioning accelerates the above process by slowly increasing the aging temperature but assuring that it always remains below the current  $A_s'$ . While  $A_s$  continues to increase, the aging temperature can be increased and the entire process significantly accelerated, reducing the total preconditioning time to under 4 days.
3. Constrained preconditioning shortens the process because of the martensite thermoelasticity. After deformation in the martensite phase, the parts can be constrained and prevented from recovering, thereby shifting  $M_s$  upwards – in principle allowing aging at temperatures up to  $M_d$ . In the subject alloy this allows aging well above room temperature, reducing the required times to under one hour.

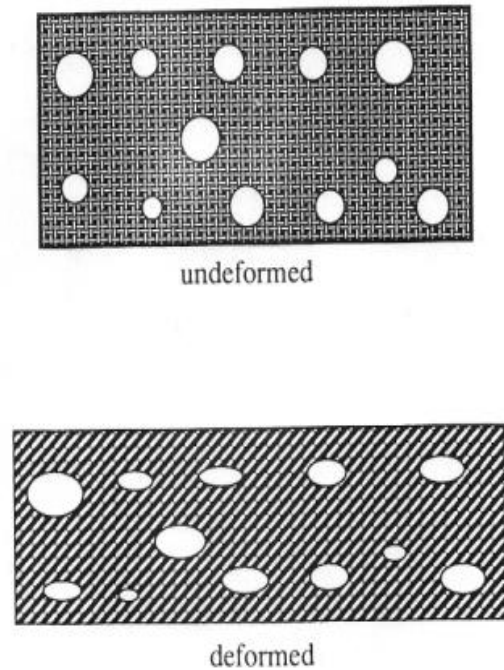
All three of the above processes can be used to shift  $A_s'$  to  $45^\circ\text{C}$  or above. For completeness one should note that there are two undesirable side effects of preconditioning:  $A_f$  is shifted even more than  $A_s$  so that the recovery response becomes sluggish, and the preconditioning has led to the development of two of the oldest and most successful shape memory products: the Permacouple (Figure 3 a) and the backshell ring fastener (Figure 3 b).



**Figure 3.** Two products made by preconditioned Cu-Zn-Al-Mn are (a) the Permacouple and (b) the backshell braid ring.

The mechanical advantages of Ni-Ti over the Cu-Zn-Al-Mn alloy, such as greater ductility, fatigue resistance, strength, creep resistance, corrosion resistance, have always made this the preferred alloy for critical couplings and fasteners even though heat-to-shrink capabilities have not been available until relatively recently. The development of this capability, in fact, has long been considered one of the keys to the widespread deployment of shape memory. Although the martensite in Ni-Ti is not susceptible to stabilization like the Cu-Zn-Al-Mn alloy, a similar sort of effect has been achieved by introducing an inhomogeneous microstructure. This is made possible the addition of some 9 at.% niobium, and then over-deforming in the martensitic phase. The niobium is essentially insoluble in the matrix, forming large volume fractions of essentially pure niobium particles. The hysteresis of these alloys is somewhat larger than that of the binary (80°C versus 30°C) when measured without applying any external stress (such as would be measured by DSC or resistivity); but when the transformation is accompanied by a shape change, the hysteresis becomes much larger (in excess of 120°C).

The microstructural mechanism responsible for the hysteresis expansion has not been entirely defined, but can be understood in general terms by considering the schematic representation of the microstructure shown in Figure 4. X-ray and TEM observations have shown that both the martensitic Ni-Ti matrix and the niobium particles undergo deformation at relatively low stresses [3].



**Figure 4.** Schematic representation of the undeformed (above) and deformed (below) microstructure of martensitic Ni-Ti-Nb. The light spherical phase represents nearly pure, very soft niobium, and the matrix represents the essentially niobium-free Ni-Ti matrix. Both phases participate in the deformation process, providing irreversible and reversible components, with the irreversible component increasing hysteresis.

The martensite deforms reversibly by the usual twin boundary motion while the niobium deforms irreversibly via slip. This partitioning of the total strain into reversible and irreversible components appears to be unique to the Ni-Ti-Nb system since we know of no other systems in which a large volume fraction of a soft second phase is formed. When the deformed composite structure is heated above  $A_s$ , the matrix phase begins to recover but can only proceed significantly by plastically reforming the niobium particles back to their original shape. Thus the irreversible deformation delays recovery, increasing  $A_s$  to  $A_s'$ . One would expect the shift in  $A_s$  to increase as the total strain increases since the irreversible strain component increases, Figure 5. One also expects and observes that the second cycle  $A_s$  (after recovery and reforming of martensite) is again original value, just as in Cu-Zn-Al alloys.

Applications made from the above described process have been commercially available since 1986. The most successful to date has been a backshell braid ring which is a welded wire ring coated on the ID with a polymer to allow electrical heating without passing the current through the substrate, Figure 6.

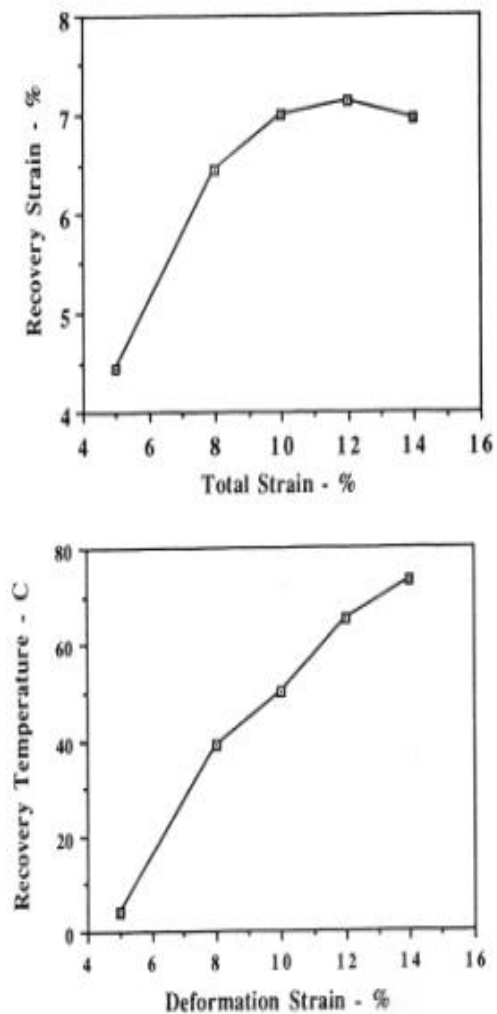


Figure 5. The effects of overdeformation on the recovery strain and the recovery temperature ( $A_s'$ ) of Ni-Ti-Nb.

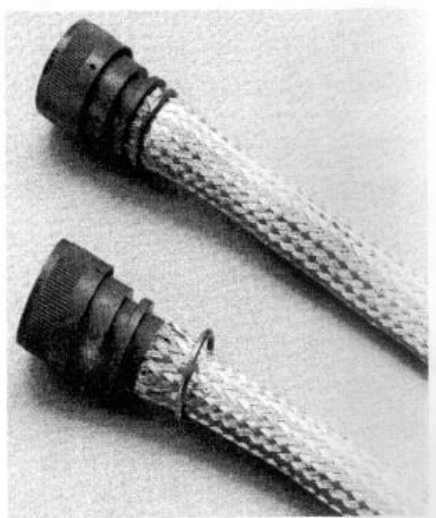


Figure 6. The first product to be made from Ni-Ti-Nb was backshell braid ring to perform similar tasks as the Cu-Zn-Al-Mn version (Figure 3 b).

### 3. CONCLUSIONS

Table 1 compares the properties of Ni-Ti-Nb with Cu-Zn-Al heat-to shrink alloys.

Table 1. Typical properties of high hysteresis alloys.

Property	Cu-Zn-Al	Ni-Ti-Nb
$M_S$ (zero load) [°C]	-40	-140
Maximum $A_s'$ [°C]	+50	+50
$\square_r$ [%]	3.5	8.0
$\sigma_r$ [MPa]	400	700
$d\sigma/dT$ [MPa/°C]	2	3.5

Although it appears at first glance that the Ni-Ti-Nb alloys are far superior, the Cu-Zn-Al alloys can be made at a far lesser cost. To date, application for the Cu-Zn-Al alloys have not been wide-spread enough to allow us to take full advantage of lower raw material costs, but the potential is there.

### 4. REFERENCES

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