

Stabilisation of Martensite in Copper Based Shape Memory Alloys

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ABSTRACT

The experimental facts on the stabilisation of martensite in copper base shape memory alloys, of interest to the scientific investigator and the practical alloy processor and user are reported. Factors that have an influence on stabilisation are considered in this respect. The mechanisms proposed in the literature to explain stabilisation are critically examined.

1. INTRODUCTION

It is well known that ageing copper base shape memory alloys in their martensitic state tends to raise the martensite to parent β phase retransformation temperature [1-4]. Diffusional processes during ageing are responsible for this shift with respect to the nominal retransformation temperature. The shift increases with the extent of diffusion. Martensite is thus stabilised with respect to the parent β phase and the effect is commonly referred to in the literature as "stabilisation (of martensite)".

As diffusion is faster at above ambient temperatures when compared to sub ambient temperatures, stabilisation is more readily observable in material that transforms to martensite above room temperature. The changes in martensite which bring about its stabilisation are, however, removed extremely quickly upon its retransformation to the β phase and the material returns to its nominal transformation characteristics gradually or abruptly depending on the alloy and the experimental conditions [1-6]. In this sense, stabilisation may be considered a temporary, removable effect through retransformation of martensite to β . This recoverability may, nevertheless, be only partial or even totally absent after prolonged ageing. In the latter event the aged martensite does not revert at all to the β phase. This is particularly notable in the presence of vacancies retained after a quench from higher temperatures. Usually tempering has set in after such ageing and the martensite structure is lost for the purposes of any diffusionless transformation.

The object of this report is to present the facts on the stabilisation of martensite, that would interest the scientific investigator as well as the practical shape memory alloy processor and user. To this end, stabilisation in this report shall imply ageing to a limit within which the stabilised martensite is still retransformable to β phase, as only such materials can be used in shape memory applications. Besides, stabilisation of β' martensites alone will be considered here, as they are the working martensites in shape memory applications. The basics of stabilisation have been reviewed earlier [7]. The present report, in

some respects, will, therefore, be repetitive. However, complimentary information will be provided here in the form of past and present results on using or countering stabilisation in practice. In addition, the mechanisms proposed so far in the literature, to explain stabilisation will be critically examined and discussed.

2. STABILISATION AND SHAPE MEMORY APPLICATIONS

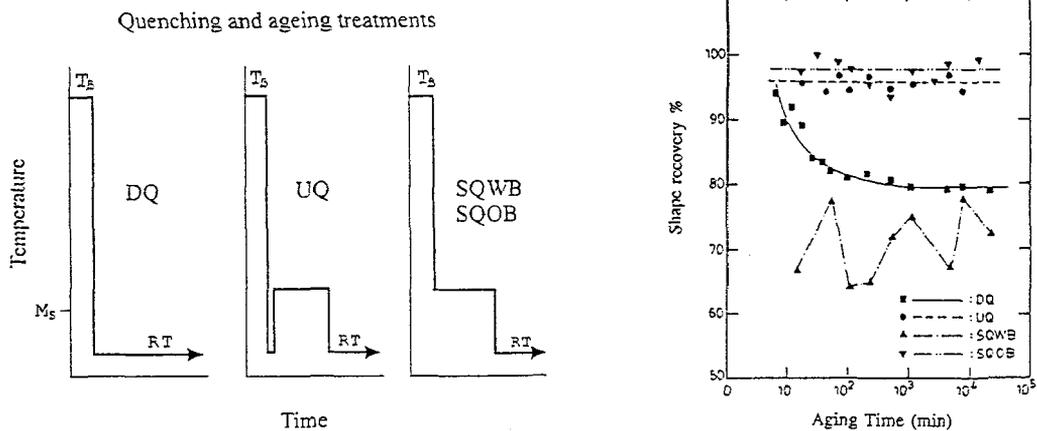
Stabilisation of martensite can be used effectively or may be unwanted depending on the shape memory application.

Stabilisation has been used effectively in preventing premature recovery of a device before installing it in its final place [1,8]. The device is a coupling, where after deformation in the martensitic condition, the assembly is allowed to warm up. It then recovers its shape and the part remains in the β condition throughout its service life and maintains the integrity of the joint, whether hermetic or mechanical, through the recovery force it exerts. It should not transform to martensite at service temperatures as this would lead to a reduction in the recovery stresses and a weakening of the joint. Alloys with M_s temperatures below ambient temperature are needed in such applications. They were originally expanded, stored and assembled in liquid nitrogen. But the stabilised martensite with its single cycle shape recovery temperature shift to higher values has eliminated the need for cryogenic storing. After substantial stabilisation (stabilised $A_s > 50^\circ\text{C}$), the expanded part can now be stored and transported, in the martensitic condition, at ambient temperatures without premature recovery. Following its final installation, by heating to retransform the stabilised martensite, the M_s temperature falls back to its original sub-ambient value, the part at ambient temperature remaining in the β condition.

Another possible use of the stabilised martensite, though not related to its retransformation, stems from the increased strength and the springback it exhibits. Energy storage and linear-temperature independent-superelastic applications could use these properties [9,10]. In most other applications, a reproducible retransformation temperature is required with cycling and time of hold in the martensitic condition. Stabilisation is unwanted in such cases and is to be inhibited.

3. HEAT TREATMENT AND STABILISATION

Stabilisation, as already noted, results from a thermally activated process. The rate and extent to which it sets in can thus be affected by the presence of vacancies introduced into the martensite prior to ageing. Copper base alloys are usually quenched to retain the β phase for further transformation to martensite.



Figs.1 & 2. Quenching and ageing treatments schematised & effect of post quench ageing on shape recovery in a Cu-Zn-Al alloy(after Leu and Hu, ref.11)

The severity of the quench and any further treatments will determine the concentration of vacancies left in the martensite to accelerate diffusion. The ageing response of a Cu-Zn-Al alloy after treatments (fig.1) designated as direct quenched (DQ), upquenched (UQ), step quenched in water bath (SQWB) or oil bath (SQOB) as reported recently by Leu and Hu [11] is shown in fig.2. Ageing DQ alloys leads to the most rapid and serious stabilisation. The retransformation of martensite to β may even be lost in this case, if the alloy transforms nominally at as high a temperature as 100°C. UQ and SQOB samples provide the most stable martensite and shape memory behaviour with time after the treatment. This has, obviously, to be related to the effectiveness in getting rid of or introducing much lesser vacancies into the martensite after the latter treatments.

Stabilisation has been reported to reach a saturation value which itself depends on the ageing temperature [12]. This saturation value has been claimed to vary on changing the ageing temperature from a lower to a higher value but not vice versa. Different stress levels during ageing have also been reported to have negligible or no influence on the extent of stabilisation [5,12].

4. ALLOY COMPOSITION, β GRAIN SIZE AND STABILISATION

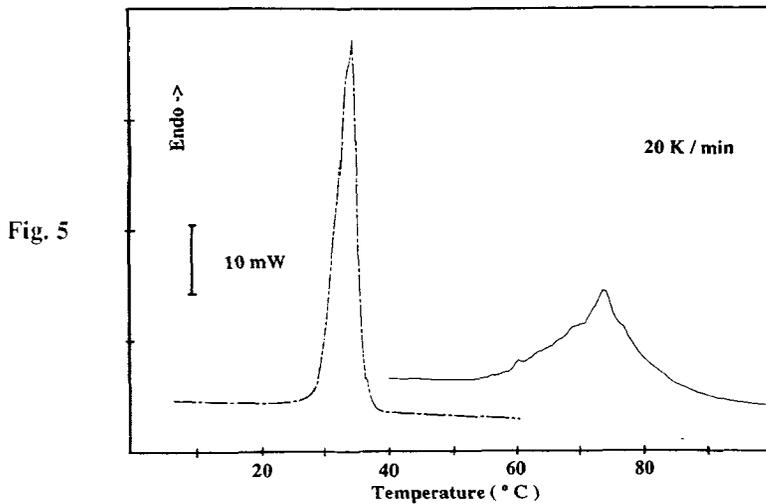
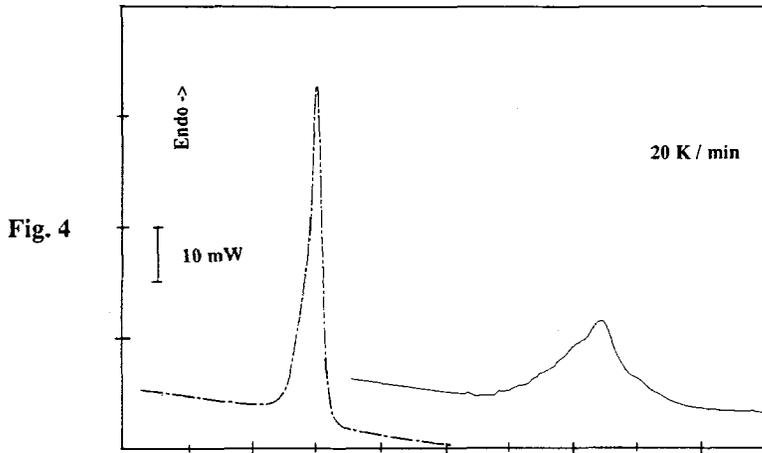
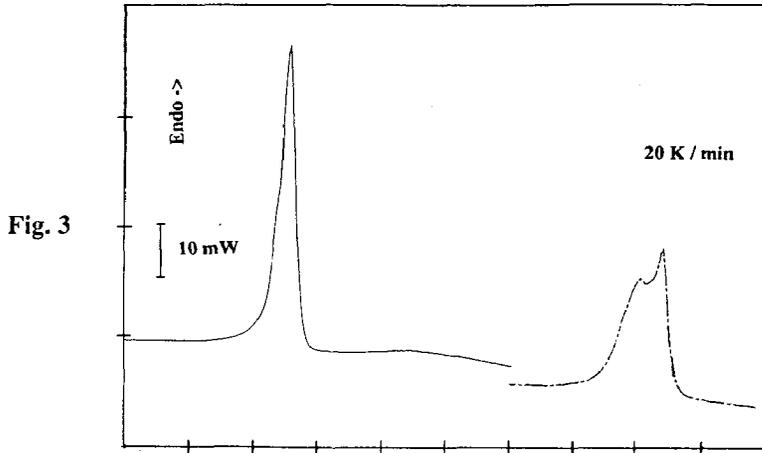
Both alloy composition and β grain size are relevant to the issue of stabilisation. If stabilisation is desired as discussed in section 2 where diffusion at relatively low temperatures is sought, this could be met through the addition of specific alloying elements [1]. With commercial Cu-Zn-Al and Cu-Al-Ni base alloys, there is also the question of the optimum aluminium content from the point of view of processing and of the stability of the martensite when subjected to ageing. A lesser aluminium content is generally preferred for reasons of easier hot deformability. A higher aluminium alloy, on the other hand, could provide a more stable martensite with respect to ageing [13]. This calls for a compromise on the aluminium content.

Cu-Al-Ni base alloys are also known to be less susceptible to stabilisation on ageing, when compared to Cu-Zn-Al alloys. This has been attributed by Kong et.al. [26], studying vacancy mobility in either alloy, to the relative immobility of vacancies and their reduced influence on diffusion in Cu-Al-Ni martensite. The stronger bonding force between Al and Ni atoms is believed by these authors to be the cause for this immobility of vacancies.

For improving their mechanical properties, copper base shape memory alloys need to be grain refined. Intuitively, the fine grained material might also be considered less susceptible to be stabilised. This stems from the reasoning that a higher proportion of grain boundaries would act as effective sinks to vacancies during any quenching, thereby reducing their concentration and subsequently contribution to diffusion which would lead to stabilisation.

5. MARTENSITE MICROSTRUCTURE AND STABILISATION

Ageing and stabilisation have been more often investigated by retransforming a collective group of martensite plates. Little attempt has been made in measuring the retransformation of a reduced number of aged martensite plates including a single plate of martensite. The results on retransformation of such aged single variant, bivalent and polyvariant martensite microstructures are presented below (figs.3-5). These results indicate that A_f temperature of the stabilised martensite microstructures are nearly the same. With reduced variants, notably with the single variant microstructure, the A_s temperature shift is a maximum and the retransformation to the β phase is relatively sharper and occurs over a narrower range of temperature. The significance of these results will be taken into consideration while discussing the mechanisms of stabilisation in a later section.



Figs. 3-5: Retransformation in DSC of stabilised monovariant (Fig. 3) and multivariant (two variants alternating - Fig. 4 - and self accommodating group of variants + fill ins - Fig. 5) martensite microstructure, compared to retransformation in the following heating cycle.

6. INHIBITION OF STABILISATION

Several methods have been used to contain the stabilisation of martensite. Step quenching, as already described, provides a means of achieving this end. It has been shown recently [14], that thermal cycling of the material also makes the martensite more stable to ageing as compared to an uncycled material. Even more positive are the results on two way memory trained materials, which tend to show as can be seen in fig.6 very little stabilisation on ageing at a relatively higher temperature for substantial times.

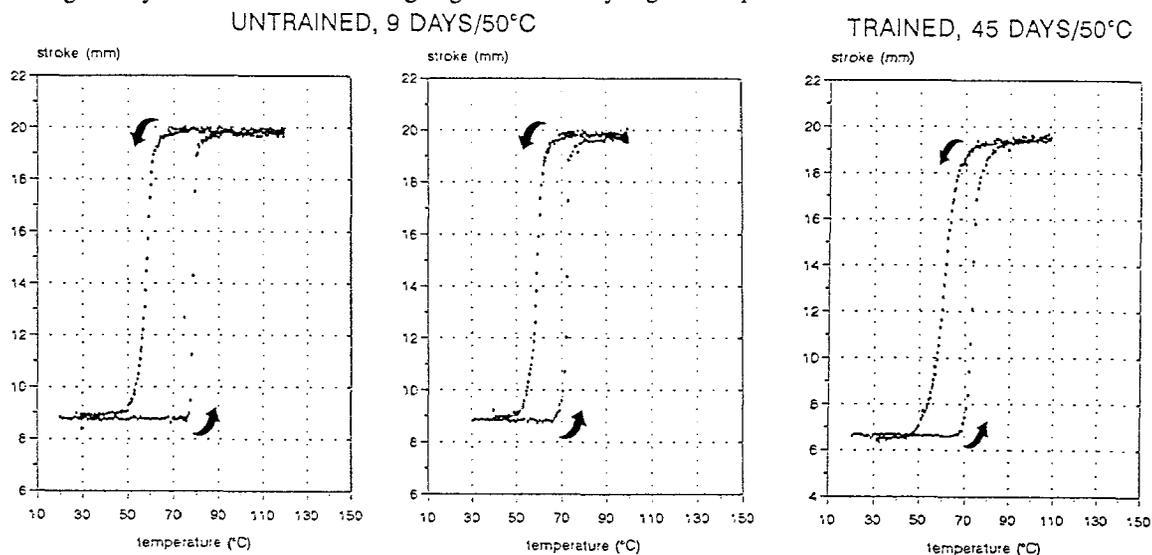


Fig.6. Effect of ageing on an untrained and a two way memory trained Cu-Zn-Al sample

But, perhaps the most interesting finding to date, on the inhibition of stabilisation, has been reported by Duan and Stobbs [15]. These authors have shown that hot rolled Cu-Zn-Al alloys are hardly stabilised even after ageing for one and a half years. Wolska, Chandrasekaran and Cesari [16] have extended this work to determine whether the temperature of rolling and the amount of deformation also play a role in inhibiting stabilisation. Their findings, summarised in fig.7, indicate that

- for a given deformation temperature, the material that is deformed more is less prone to stabilisation
- for a given amount of deformation, the material that is deformed at a lower temperature suffers lesser stabilisation.

In other words, higher amounts of deformation and lower deformation temperatures provide the best combination to inhibit stabilisation.

7. STRUCTURE AND MICROSTRUCTURE CHANGES DURING AGEING

X-Ray and electron diffraction investigations conducted at different stages of ageing and thus stabilisation have confirmed a gradual change in the lattice parameters of martensite. The "a" parameter rises and "b" falls while the order dependent monoclinic angle of the structure increases towards 90° [17]. Additionally, several authors [18,19] have reported changes in the stacking fault density within a martensite plate, brought about most likely during ageing by the interaction between the excess vacancies and the faults.

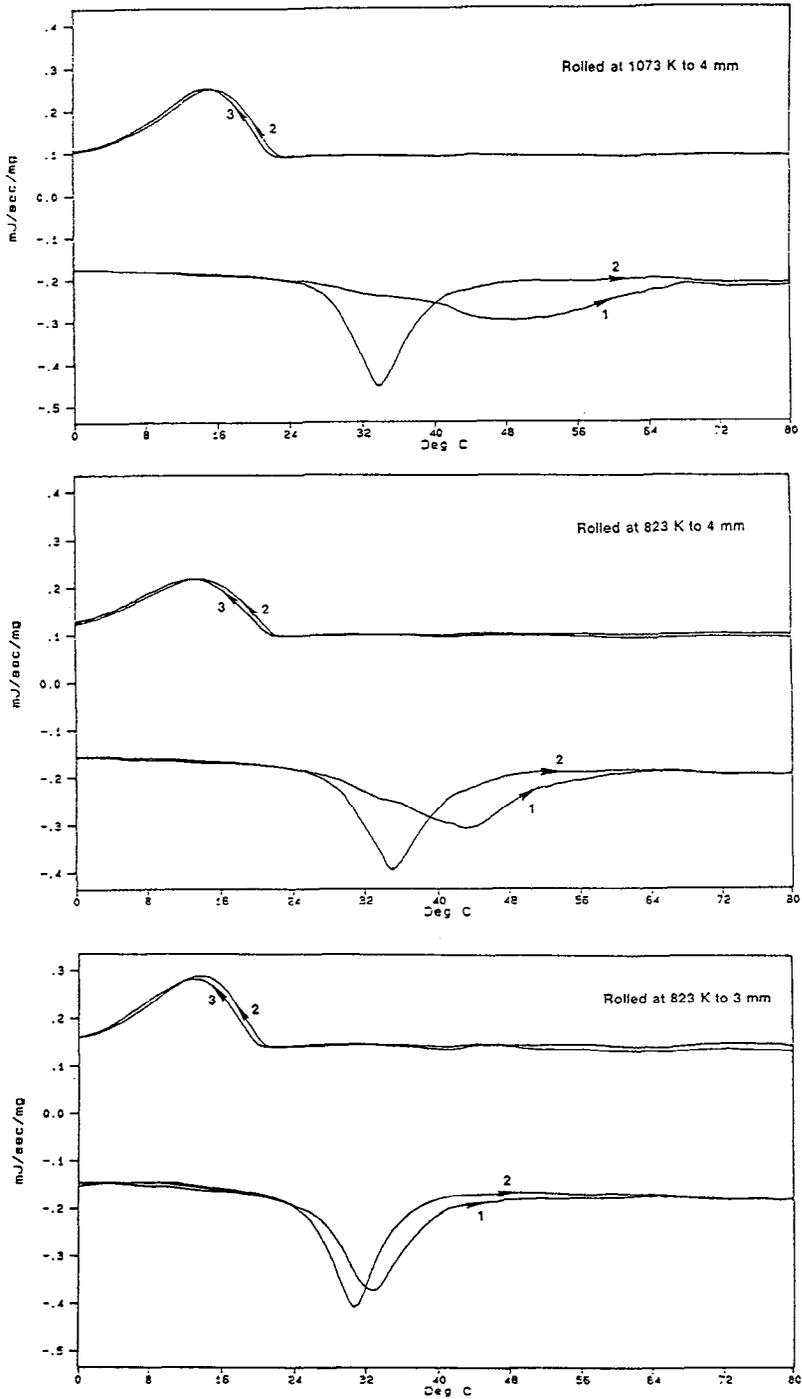


Fig. 7. DSC curves of transformation behaviour after ageing in the martensitic condition alloys previously hot rolled

8. MECHANISMS RESPONSIBLE FOR STABILISATION - A CRITICAL EXAMINATION

Based on observations of stabilised martensite or its retransformation and subsequent transformation, several explanations of stabilisation have been put forward [2-7,12,14-27]. They can be broadly divided into two groups - 1. atom relaxations and resulting strain energy changes near interfaces and defects in the martensite (often this has been referred to as "pinning" in the literature) 2. atom rearrangements in the martensite volume occurring during ageing.

The pinning mechanism was proposed at the very outset based on internal friction measurements on the stabilised martensite [2,28]. Such measurements indicated a substantial reduction in the damping capacity of the overall microstructure. This was construed as due to vacancy pinning of martensite-martensite interfaces and the consequent loss in the mobility of such interfaces. Be as it may be, this does not necessarily inform us as to why the retransformation of the stabilised martensite should be shifted to higher temperatures. If, pinning of interfaces is primarily responsible for the raised retransformation temperatures of the stabilised martensite, it would have to be established that the β - martensite interfaces are pinned. This is, however, not evident from published data.

Alternatively, stabilisation could be considered as due to the difficulty of nucleating the β phase at the pinned martensite-martensite interfaces. If so, this should affect the A_s temperature primarily, the A_f remaining that of an unaged martensite. Notwithstanding, it is often the A_f temperature that is shifted to much higher values after stabilisation. There is, however, one interesting experimental observation (fig.8) after partial retransformation of stabilised martensite, as reported by Scarsbrook, Cook and Stobbs [18], that keeps these mechanisms still open to discussion. This relates to the appearance of conjugate habit planes corresponding closely to mutually perpendicular β {110} planes which terminate on each other. It has been suggested that the normal habit plane is from the reversion of unstabilised martensite, whereas the equivalent perpendicular habit plane is from the reversion of the stabilised martensite at a higher temperature. This microstructural state could be indicative of β nucleation and subsequent growth problems. But, it could also be interpreted as if alternate routes to nucleation and growth of β are available at relatively low superheating, unless it can be shown that the observed microstructural state is the one primarily responsible for large shifts in A_s and A_f .

Another interesting possible contribution to stabilisation, from the observed decrease in stacking fault density in martensite upon ageing, has been pointed out by Nakata et. al. [19]. These authors explain that such decrease in stacking fault density, takes away a part of the lattice invariant shear thus preventing the reverse transformation of martensite to β . This would have to be supplemented, they argue, by an extra driving force to introduce a new shear, leading to the observed stabilisation. Nevertheless, the authors do not consider this mechanism to be the primary reason for martensite stabilisation as the decrease in stacking fault density cannot be correlated well with the degree of stabilisation.

The alternative mechanism of stabilisation, that due to configuration changes produced on ageing the martensite, derives its support from the observed lattice parameter changes of martensite with ageing [17]. The mechanism is related to a bulk or volume rather than any interfacial effect. It is based on the concept that in the stabilised condition, the free energy of the martensite phase is lowered relative to that of the austenite phase (with the corresponding atom configuration). The best evidence for this concept and mechanism is obtained by following the forward β -martensite and reverse transformations immediately after the reversal of the stabilised martensite. This must, nevertheless, be carried out by avoiding, as far as possible, diffusion in the β phase, which can otherwise erase the corresponding changed configuration inherited by that phase. The maximum temperature of the reverted stabilised martensite should thus not be allowed to exceed 0°C or preferably even a lower temperature. If the subsequent transformations under such experimental conditions exhibit a tendency for a gradual return over a few cycles to the nominal - unstabilised martensite condition, this can be considered as the most convincing evidence for configurational changes in the martensite volume with ageing as being responsible for stabilisation. On the other hand if the subsequent transformations become coincident with the nominal transformation paths

without any shifts, then it would be a good indication of the so called pinning mechanisms being operative.

The gradual return to nominal unstabilised transformation explained above has been convincingly demonstrated (figs.9a and 9b) in both stress induced as well as thermal-spontaneously induced stabilised martensites [5,6]. A number of other observations, would lend credence to the mechanism of configuration changes with ageing, most often though by negating the pinning mechanism. Plate refinement increasing the number of martensite-martensite interfaces and augmentation of dislocations with thermal or two way memory cycling and plastic deformation (rolling) should in principle provide more opportunities for pinning and enhancement of stabilisation. Yet, to the contrary, inhibition of stabilisation is promoted after such changes. All evidences thus favour the configuration changes in the martensite with ageing as the primary mechanism causing stabilisation.

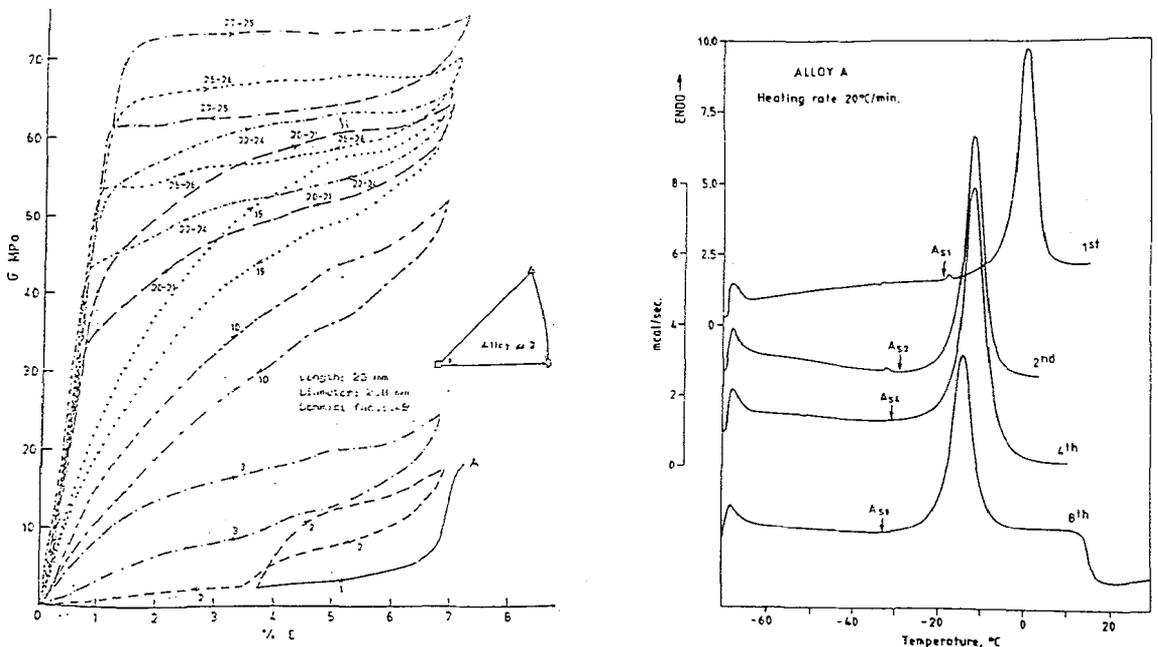


Fig.9. Gradual return to nominal transformation behaviour after retransformation of stabilised martensite in (a, left) stress induced Cu-Zn-Al martensite (after Abu Arab et.al., ref.5) and (b, right) thermally induced Cu-Zn-Si martensite

Stabilisation was originally suggested [12] as occurring due to the interchange of first neighbour copper and zinc atoms in Cu-Zn-Al. This has been confirmed recently [19] by ALCHEMI experiments using the electron microscope. But even as one agrees that atom rearrangements on ageing the martensite are responsible for its stabilisation, there have been arguments in the literature whether ageing tends to relatively disorder or order the martensite [12,22,24]. The following results and arguments could be taken as supporting the relative disordering of martensite on ageing.

Quenching the alloys from higher and intermediate temperatures is known to lower the martensitic transformation temperatures. The effect has been attributed to a relatively disordered β transforming to martensite [30]. Such a β stabilisation and the order can also be recovered, like martensite stabilisation, by a subsequent hold in the β state. But, when the quenched sample is aged in the martensitic state, it leads to stabilisation of the martensite with respect to the lowered transformation temperatures. After

retransformation of this stabilised martensite in subsequent cycles, the transformation temperature first approaches the lower β stabilised value and then increases in subsequent cycles with recovery of order to the nominal value. The effects of martensite stabilisation would thus seem to be recovered first and independently from the effects of the β stabilisation. This need not be expected if the martensite stabilisation produces relative disorder while recovery after β stabilisation corresponds with relative increase in order.

Nevertheless, the saturation stabilisation mentioned in section 3 has been attributed to an equilibrium degree of order attained at the temperature of ageing [12]. The change in saturation value only on increasing the ageing temperature and not on reducing it, though, has not been clarified yet. Besides, the quantitative models based on interchange of atoms to explain stabilisation [12] assume that the entropy of the martensite transformation is unchanged in spite of such changes. Experimental evidence has been provided [29] to show that this assumption is not strictly true and that with increasing stabilisation the transformation entropy tends to decrease.

9. FURTHER COMMENTS ON STABILISATION AND ITS INHIBITION

Earlier the relevance of the martensite microstructure on its retransformation after it is stabilised was presented in figs:3-5. The single variant martensite retransformed rather sharply with both A_s and A_f shifted equally to higher values. The bivariant and polyvariant stabilised martensites retransformed over a broader temperature range, with A_s near nominal-unstabilised values but A_f shifted to higher than nominal value. The presence of interfaces in the latter cases or in cases where the retransformation is partial and incomplete would not again favour necessarily, the pinning mechanisms again in explaining these results. They can very well be explained, based on arguments given below, on the basis of configuration changes in martensite as the primary mechanism causing stabilisation.

One has to consider that martensite plates have been stabilised in an inhomogeneous way. In other words, different plates have been stabilised to different extents because of different amounts of diffusion in them. This complex situation is brought about by the specific conditions of temperature, stress and amount of defects prevalent at the time of formation of a given plate of martensite. Typically during a quench through the M_s and M_f , the martensite plates that form first in the β phase would be inheriting more vacancies than the plates which form subsequently. The last formed plates, which are usually the so called "fill ins", would be forming under conditions of higher elastic stored energy which provides them with a higher driving force to retransform. Also, we have seen already how plate refinement and presence of line defects can inhibit stabilisation. The last formed plates are indeed finer and are possibly associated with proportionately higher quantity of line defects. The last formed plates, as is the general behaviour of martensites, are the first to retransform. All these factors would promote the first formed plates to be more stabilised upon ageing than the plates forming later. The A_s temperature after ageing would thus be close to the unstabilised-nominal value whereas the A_f temperature would have shifted to considerably higher values. It can also happen that structural rearrangements within the martensite plates may have proceeded to the extent that the resulting structure is no more martensitic and cannot be reverted anymore in a diffusionless manner to the parent β phase. The structure at this stage would be best considered as that of tempered martensite. This would account for the incomplete reversions or even complete absence of any retransformation of the martensite to the parent β phase

Stabilisation is inhibited in the presence of an enhanced quantity of line defects. This is possibly because the latter act as sinks and reduce the amount of vacancies that could otherwise accelerate and contribute to diffusion. Nevertheless, not all kinds of dislocations would seem to inhibit stabilisation, as Duan and Stobbs [10] have reported that dislocations introduced by low temperature fatigue do not seem to achieve inhibition as much as rolling does. Dislocations in ordered materials do tend to introduce some disorder. The crystallographic analysis of such dislocations either inherited by or created in the martensite and a more quantitative understanding of their role in inhibition would be worth investigating.

CLOSURE

Stabilisation of martensite in copper base shape memory alloys can be useful in limited applications. For other applications, where stabilisation is to be inhibited, hot rolling at a lower temperature in the β phase with as large a reduction as possible and thermal or two way memory cycling can be of benefit. Alloy composition, grain size, martensite microstructure and defects have an influence on stabilisation. The primary mechanism responsible for martensite stabilisation is a change in the atomic arrangement within the martensite that occurs on ageing.

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