

The Effect of Stress Ageing on the Properties of Shape Memory Alloys

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ABSTRACT

The performance characteristics of shape memory alloys operating in an overtemperature shut-off valve at a temperature of 95°C for up to 2000 hours are presented. Alloys of NiTi, Cu-Al-Ni and Cu-Zn-Al have been characterised under these ageing conditions. The effect of altering the processing parameters, viz solution treatment temperature, quenching technique and training procedure were examined. All alloys show degradation of the memory behaviour but results are presented which demonstrate that improvements in degradation can arise by altering the solution treatment temperature and training procedure.

BACKGROUND

A potential client approached Memory Metals Limited with a request for incorporating a memory metal spring as an overtemperature shut-off valve in his product. The client stipulated that the following parameters must apply.

- The operating temperature to be 95°C and the spring would be exposed to this temperature for periods of up to 350 hours.
- At 95°C the spring to deflect 6mm and exert a force of 7N.
- A life cycle of 2000 hours at 95°C.
- Cost would be an important criteria in the selection of memory metal for this application.

1. INTRODUCTION

There were three commercial alloys that could be considered for this application, viz NiTi, Cu-Al-Ni and Cu-Zn-Al. For NiTi and Cu-Zn-Al the operating temperature of 95°C is close to the maximum operating temperature recommended for these alloys. Their preferred use at these temperatures is in single or low cycle applications because on cycling the transformation temperature tends to walk to higher temperatures [1]. However, Cu-Al-Ni memory alloys are known to have better thermal stability at this temperature [2]. Unfortunately, the mechanical processing characteristics of Cu-Al-Ni alloys do not compare as favourably as those of Cu-Zn-Al and are not so good as NiTi due to the presence of brittle γ

precipitates [3]. Also, Cu-Al-Ni alloys are not as widely commercially available as the other two memory alloys.

Although this background knowledge on the behaviour of memory alloys at 95°C was known, data on their ageing characteristics at this temperature for the conditions met in this application did not exist. Therefore, in order to select the memory alloy most suitable for this application, a test programme on the performance of these alloys proved necessary.

As the cost of the memory spring was to be an important parameter in the final selection of the alloy system, the test programme was set up so as to consider the effect of processing parameters on the ageing characteristics. The processing parameters examined were solution treatment temperature, quenching technique and training procedure.

For NiTi alloys a training cycle of 100 cycles is recommended for stabilising the memory characteristics particularly where cycle life is important [4]. However, for this application the ageing characteristics rather than the cycling behaviour at 95°C were more important and therefore fewer training cycles may have proved acceptable.

The standard training cycle for copper-based alloys to achieve stability and two way memory is 10 cycles through the transformation band. There have been reports [5,6] that training techniques involving no cycling but ageing the memory alloy under stress (stabilised stress induced martensite training) results not only in two way memory without any training cycles but also in an improvement in the stability of the A_s temperature on subsequent cycling [7].

A further technique for improving the stability of the A_s temperature in copper-based alloys is by adjustment of the solution treatment temperature. This results in a duplex $\alpha\beta$ structure [8].

2. EXPERIMENTAL

The memory alloys required an A_s temperature of 80 to 85°C in order to achieve the operating parameters of the product. In Table 1 the chemical composition of the memory alloys investigated are given.

Table 1 Alloy Compositions

Alloy	%Ni	%Ti	%Cu	%Zn	%Al	%Ni
1	53.90	46.10	-	-	-	-
2	-	-	81.80	-	13.50	4.70
3	-	-	73.70	20.62	5.68	-

To achieve the required A_s , the NiTi springs were heat treated at two different temperatures; the untrained springs were heat treated at 425°C and the springs to be given training cycles were heat treated at 500°C. This is necessary since during the first few training cycles, the A_s temperature shifts to lower temperatures and then stabilises.

The Cu-Zn-Al springs were given the following treatments.

SSMC19 Standard treatment. Solution treated at 800°C, step quenched to 100°C and air cooled to room temperature. Trained by cycling between 20°C to 150°C.

SSM1 As SSMC19 but no cycling; spring compressed so that it was open to 30% of its fully open state and stress aged at 150°C for 30 minutes.

SSMC1 After step quenching to 150°C, the spring was compressed to its coil bound state at 150°C and stress aged for 30 minutes.

AB5 As sample SSMC19 but solution treatment temperature 620°C.

Cu-Al-Ni springs were heat treated at 800°C, water quenched to room temperature and aged at 150°C for 1 hour. They were trained by cycling between 20°C and 150°C

Springs were trained by cycling against a bias spring having a spring rate of 1.2N/mm with a preload of 0N and 4N for the copper-based alloys and the NiTi alloy, respectively. The NiTi spring required a preload of 4N in order to return to its coilbound state on cooling to room temperature.

Using the same bias springs and preloads, the springs were aged at 95°C for 2000 hours in a water bath. At various time intervals upto 2000 hours, the springs were removed from the water bath and their deflection measured at 95°C.

3. RESULTS

Figures 1 and 2 show the deflections of the test springs as a function of ageing time for the NiTi and copper-based alloys, respectively. For the NiTi alloy, the importance of the training cycles prior to ageing is clearly demonstrated; with no cycles there is a large reduction in deflection on ageing which is reduced as the number of training cycles increases.

Prior to ageing, all the copper-based alloys exhibited two way memory. The effect of stabilised stress induced martensite training results in a reduction in the initial deflection; the reduction being greater for the spring stress aged in its fully coil bound state.

It is well established that Cu-Al-Ni alloys exhibit better high temperature stability than Cu-Zn-Al alloys and this is borne out by the results presented in Figure 2.

Table 2 Degradation results for NiTi

Training Cycles	% Degradation
0	72.7
25	46.5
50	28.9
100	22.9

Table 3 Degradation results for copper-based alloys

Alloy	Sample	% Degradation
Cu-Al-Ni	-	23.7
Cu-Zn-Al	SSMC19	87.1
Cu-Zn-Al	SSM1	84.9
Cu-Zn-Al	SSMC1	75.5
Cu-Zn-Al	AB5	57.3

In Tables 2 and 3 the % reduction in deflection (ie. % degradation) on ageing for 2000 hours is shown for the different alloys and different treatments. For the NiTi alloy, with increasing number of training cycles, the % degradation decreases. The Cu-Al-Ni alloy shows less degradation than the Cu-Zn-Al alloy even after the modified thermal mechanical treatments. In fact, the Cu-Al-Ni alloy compares favourably with the NiTi alloy after 100 training cycles in that the % degradation is similar. From Table 3,

it would appear that ageing stabilised stress induced martensite trained material and a duplex structure of $\alpha\beta$ does improve the degradation characteristics of Cu-Zn-Al alloys. The most improvement being achieved in the duplex structure.

After the ageing tests at 95°C had been completed, all test springs were given one cycle upto 150°C. Both the NiTi and Cu-Al-Ni springs recovered the degradation that had occurred on ageing at 95°C. The Cu-Zn-Al springs showed no such recovery in their deflection behaviour.

4. DISCUSSION

The degradation characteristics of the three memory alloys under the conditions examined in this investigation show them to be different. In the case of NiTi and Cu-Al-Ni alloys, degradation is due to the upward movement of the transformation temperature to higher temperatures on ageing. For the NiTi alloy, as the degradation decreases with increasing number of training cycles, a more stable transformation temperature occurs thus resulting in a reduction in the degree of upward movement on ageing. However, for Cu-Zn-Al alloys, this upward movement appears not to occur and would indicate that the degradation arises due to structural changes taking place in the β phase, either the ordering of the β is affected or the bainite structure forms on ageing.

From the results presented both solution treatment temperature and training procedure affect the degradation of the Cu-Zn-Al alloy. Lowering the solution treatment temperature results in a duplex structure of $\alpha\beta$. An electron micrograph of the duplex structure is shown in Figure 3 which shows the form and distribution of the α . Its appearance is blocky and is frequently but not exclusively associated with the β grain boundaries. An example of such an α grain is marked at A. It would appear that the presence of the α modifies the change in the ordering of the β or affects the rate of formation of the bainite. The presence of α in the β results in the zinc and aluminium content of the β phase increasing and therefore the chemical composition of the β is altered. This would be expected to affect both the ordering of the β and the formation of bainite. For this supposition to be correct, the slight improvement in degradation achieved after stabilised stress induced martensite training should arise from the same cause, i.e. precipitates within the β . It has been reported [9] that this training technique results in the precipitation of the γ phase; it is the strain fields associated with the γ precipitates which gives rise to the stabilised stress induced martensite which produces two way memory without any thermal training cycles. In the electron micrograph (Figure 4) for sample SSM1, localised strain centres (marked at A) evenly distributed in the β were found and these are believed to be the γ phase. However, in sample SSMC1 which showed a slight improvement in degradation compared with samples SSM1 and SSMC19, the presence of γ precipitates was not detected, but the presence of a tweed structure was found. The presence of γ precipitate or the tweed structure was not detected in sample SSMC19 given the standard treatment, and therefore, it is concluded that their presence in the stabilised stress induced martensite trained samples affects the composition of the β phase. If so, this supports the argument that it affects the ordering reaction or the formation of bainite.

The rate of formation of the γ phase will depend upon a diffusion process. This is affected by the stress applied during stabilised stress induced martensitic training since in the spring given the standard treatment no γ phase or tweed structure was detected. A quenching temperature of 150°C compared with 100°C will result in a lower vacancy concentration and this in turn will affect the diffusion rate and hence the formation of the γ phase. Therefore, the difference in the structures for springs SSM1 and SSMC1 is due to the initial vacancy concentration prior to stabilised stress induced martensitic training.

5. CONCLUSIONS

This investigation has shown that three memory alloys, NiTi, Cu-Al-Ni and Cu-Zn-Al with an A_s of 80 to 85°C degrade on ageing at 95°C for 2000 hours. In conjunction with this test programme, the client

established from in-situ tests on the overtemperature shut-off valve with memory alloy springs that some degradation could be tolerated. Consequently, either the NiTi alloy after 100 training cycles or the Cu-Al-Ni alloy would be acceptable for this application. Unfortunately, both NiTi and Cu-Al-Ni alloys are expensive and with their difficulties in fabricating and processing springs, the resultant cost was not quite within the limits set by the client. This has resulted in the original volume estimates for fitting a memory alloy spring for this overtemperature shut-off valve being reduced.

A spring made from Cu-Zn-Al would be more appropriate for this application because cost would not be a constraint due to the ease of fabricating and processing springs from this memory alloy. Whilst this investigation has shown that improvements in the degradation behaviour can be achieved by altering the solution treatment temperature, quenching technique and training procedure, the improvements are insufficient to enable a Cu-Zn-Al alloy to be used in this application.

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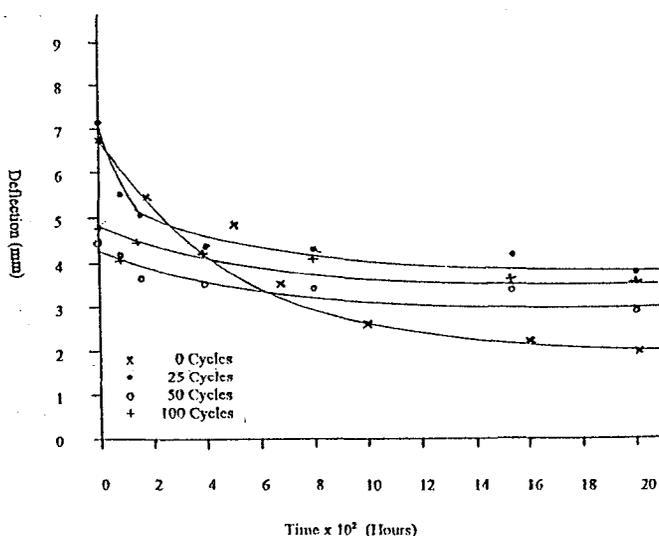


Figure 1. Ageing curves for NiTi alloy.

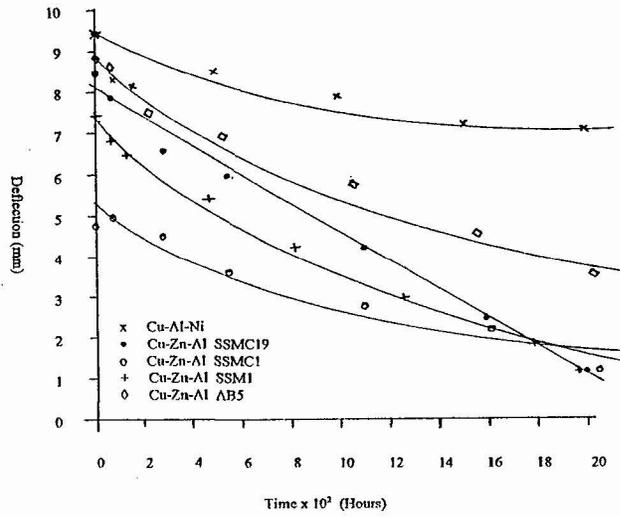


Figure 2. Ageing curves for copper-based alloys

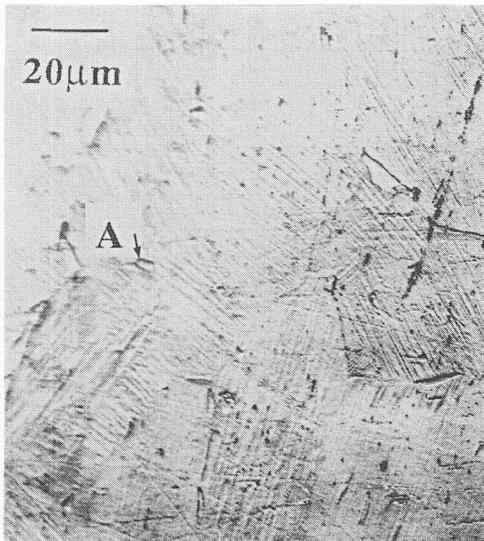


Figure 3. Duplex structure $\alpha\beta$ in sample AB5

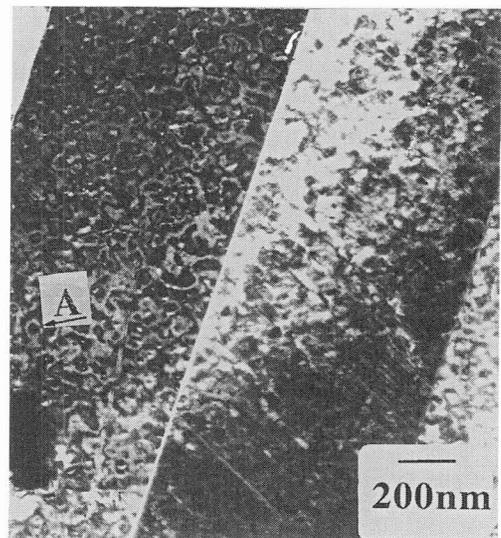


Figure 4. γ Phase (marked A) in sample SSM1