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Effect of NiAl precipitation on shape recovery of CuZnAlNi alloy

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In a CuZnAl alloy containing 2.2 wt% of nickel it was found that due to alloy quenching and low temperature ageing, precipitation of NiAl disperse particles takes place resulting in raising of martensitic transformation characteristic temperatures. The ease with which this phase precipitates indicates the low thermal stability of this alloy. At the same time the process of precipitation of NiAl particles offers an opportunity for control of shape recovery temperature by varying quenching temperature, cooling rate and especially ageing time, since variations of characteristic temperatures as a function of ageing time can be expressed by the relation $\Delta T = At^{0.5}$. It was also ascertained that the two way shape memory effect, as opposed to the one-way effect, is sensitive to processes associated with alloy ageing and also matrix phase transition in the bainite.

1. Introduction

The relatively low mechanical properties of CuZnAl alloys in comparison with those of NiTi alloys result from growth of the β-phase grains during heating at the temperature at which quenching takes place. This adverse situation may be improved by grain refinement of alloy in order to obtain a fine grained microstructure and enhanced mechanical properties [1, 2]. A separate problem arising in the technology for producing these alloys is their plastic working. This may be achieved by choosing a chemical composition for the alloy such that decomposition of the β-phase takes places via the $\alpha + \beta$ phase region where the α-phase exhibits high plasticity. Then quenching from this area leads to an alloy structure exhibiting good plastic properties enabling cold working [3]. Introducing to the alloy a small quantity of nickel also improves plasticity, making it suitable for practical applications [4, 5]. The presence of nickel, however, causes a change in alloy structure [6].

The purpose of the studies reported here was to determine the influence of the addition of nickel in a modified CuZnAl alloy on the process of precipitation of NiAl phase and also the influence on shape memory.

2. Materials and methods

A hypo-eutectoid Cu–25.35 wt% Zn–3.87 wt% Al–2.2 wt% Ni alloy modified with titanium and boron (0.27 wt% Ti, 0.04 wt% B) was chosen to be investigated. The alloy was obtained from metals of technical purity in an induction furnace. After homogenizing rods of diameter 8 mm were extruded from the ingot and, from these, wire of diameter 0.5 mm was drawn, or alternatively strips of thickness 0.7 mm were obtained by rolling.

The samples were subjected to heat treatment in a broad range of quenching temperatures applying various cooling rates together with ageing above temperature A_f.

Structural analysis consisted of optical and electron microscopy and X-ray phase analysis. Additionally, differential thermal analysis measurements and also measurements of mechanical properties were carried out. Degree of shape recovery was tested by bending a sample by an angle of 90° on a cylinder of determined diameter. The two-way shape memory effect was induced by the method described by Perkins and Sponholz [7].

3. Results

3.1. Influence of quenching temperature on alloy structure and properties

The temperature of alloy quenching from the two-phase region governs the quantity of α-phase formed. The α-phase ensures the obtaining of good plastic properties making possible cold working. Test results are shown in Table I. Alloy quenching from temperatures 500–650 °C leads to the obtaining of three-phase $\alpha + \beta +$ NiAl structure. In this state the alloy exhibits high plastic properties while maintaining high strength properties. NiAl phase particles were observed both in the α and β-phase, initially small, appearing in the form of small rods which with increasing temperature of quenching tend to grow and coagulate (Fig. 1). These precipitates exhibit some crystallographic relationships with both the α-phase and β-phase. The visible interface dislocation indicates partial coherence between the already large NiAl particles and the β-phase matrix. This is associated with the existence of a parallel crystallographic relation

TABLE I Influence of quenching temperature on phase composition of alloy, degree of shape recovery (η), characteristic temperatures and also R_m and A_{50}

Quenching temperature (°C)	Alloy phase composition	η (%)	R_m (MPa)	A_{50} (%)	M_s (°C)	M_f (°C)	A_s (°C)	A_f (°C)
500	α, β, NiAl	–	–	–	–	–	–	–
550	α, β, NiAl	–	629	16.2	–	–	–	–
600	α, β, NiAl	–	601	20	–	–	–	–
650	α, β, NiAl	–	600	16.3	–	–	–	–
700	β'_1, β_1, α, NiAl	92	–	–	19.4	− 16.5	15.2	50
750	β'_1, α	94	–	–	45.7	11	36.2	65.1
800	β'_1	95	711	2.4	50.9	19.5	42.2	65.2
850	β'_1	95	651	1.8	–	–	–	–

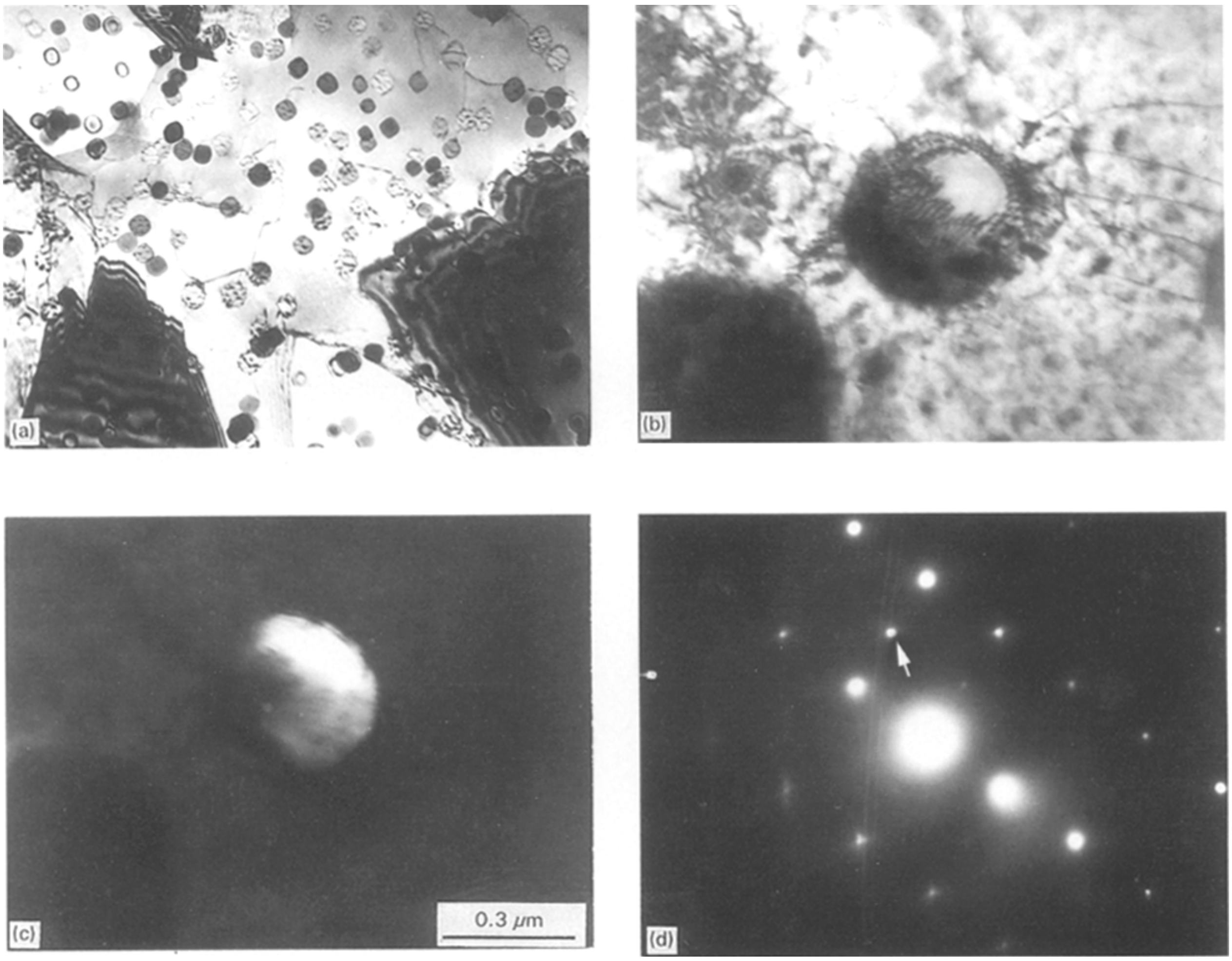

Figure 1 Precipitates of NiAl phase on the background of α-phase after cooling from 500 °C (a) and β-phase after cooling from 650 °C (b–d); (c) image in the dark field in the $1\,1\,1_{NiAl}$ reflection; (d) electron diffraction pattern of orientation $[1\,1\,0]_{\beta}//[1\,1\,0]_{NiAl}$.

and very slight differences in lattice parameters of these phases [8, 9]. Heating the alloy to temperatures above 700 °C leads to single β-phase structure. During quenching, coherent particles of NiAl phase (Fig. 2) precipitate from the solution.

Final matrix structure is the martensitic β'_1 phase of M18R structure where $\beta = 88\,°46$ minutes. Owing to the existence of strain contrast from the NiAl particles in the particular martensite plates a marked decrease of the characteristic contrast coming from stacking faults is observed. These precipitates are visible on thin foils, in the dark field in the reflections from the B2 type structure, and hence in the reflections also from the superstructure in the β_2-phase which is next inherited by martensite (Fig. 2). Identification is additionally hindered by the very nearly equal values of lattice parameters of these phases. The presence of coherent particles of NiAl phase in the CuAlNi alloy after hot water cooling [10, 11] or during ageing at 350 °C [12] has been reported.

Starting from the quenching temperature of 700 °C the alloy is in the martensitic state and exhibits shape memory. The minor quantity of equilibrium α-phase (Fig. 3) has no appreciable effect on degree of shape recovery but it does influence the temperature of shape recovery (Fig. 4). Apart from the α-phase, the

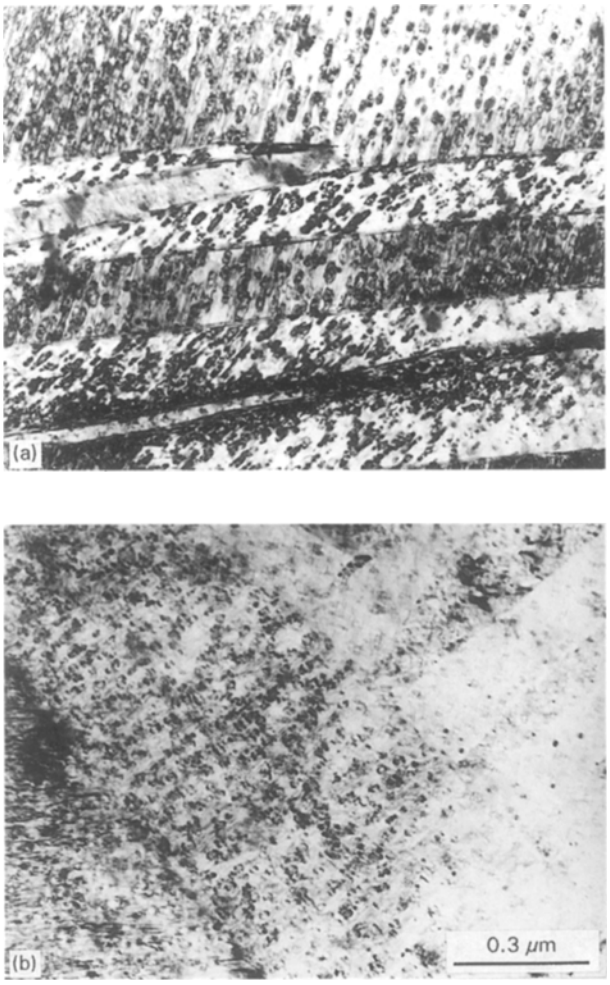

Figure 2 Dispersive precipitates of NiAl phase in the martensite.

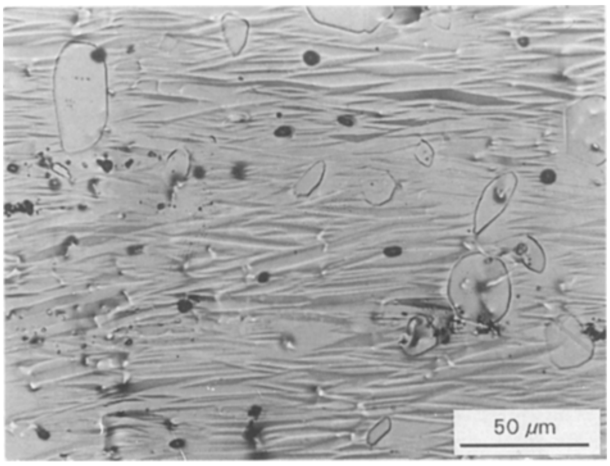

Figure 3 Alloy structure after quenching from 700 °C.

presence of trace quantities of NiAl phase exerts an influence on shifts in characteristic temperatures.

3.2. Influence of temperature and ageing time

Ageing of the alloy quenched from a temperature of 800 °C in ice water was carried out in the temperature range from 50–400 °C for a time of 1 h. From microscopic examination it was found that ageing at

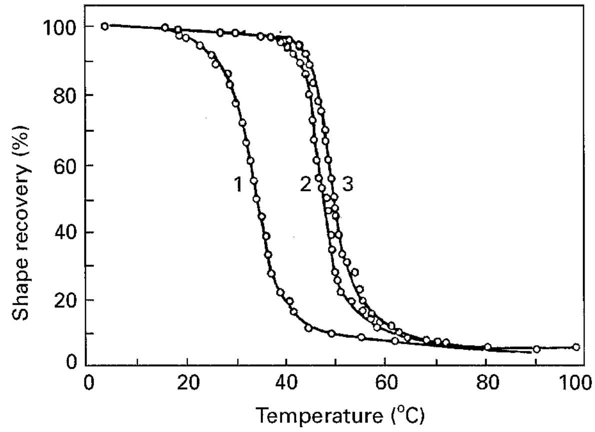

Figure 4 Changes in degree of shape recovery after quenching from temperatures: 700 °C (1), 750 °C (2), 800 °C (3).

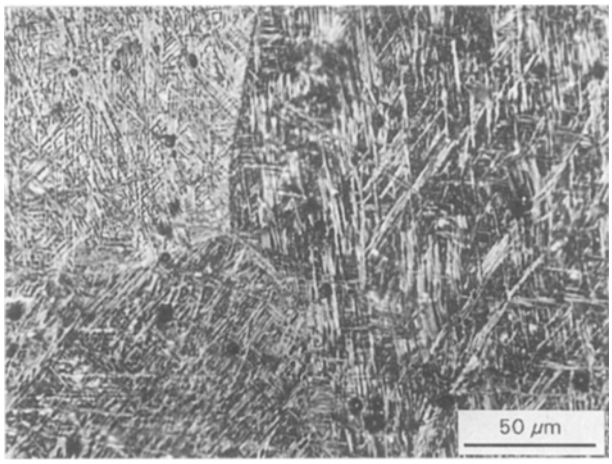

Figure 5 Alloy structure after ageing at 200 °C for 1 h.

temperatures above 150 °C causes distinct changes in alloy structure (Fig. 5). These changes are seen as considerable refinement of alloy structure and also disappearance of the self-accommodating groups of martensite plates. From the X-ray diffractograms the disappearance of certain lines coming from the M18R martensite was visible and instead the new lines appeared were attributed to 9R martensite structure (Fig. 6). Electron microscope examination of thin foils showed that these changes are caused by the formation of bainite structure (Fig. 7). The existence on the electron diffraction patterns of reflections elongated in particular directions gives evidence of the presence of stacking faults in the bainite plates. Structural changes associated with ageing temperature have a specific influence on the mechanical properties, characteristic temperatures of transformations and on shape recovery (Table II).

The data indicate the stability of shape recovery up to temperature 150 °C. However, there also takes place a narrowing of the temperature ranges of martensitic transformation ΔM and ΔA to 14 and 11 °C, respectively, indicating a reduction in number of lattice defects and in lattice friction resistance to the transformation.

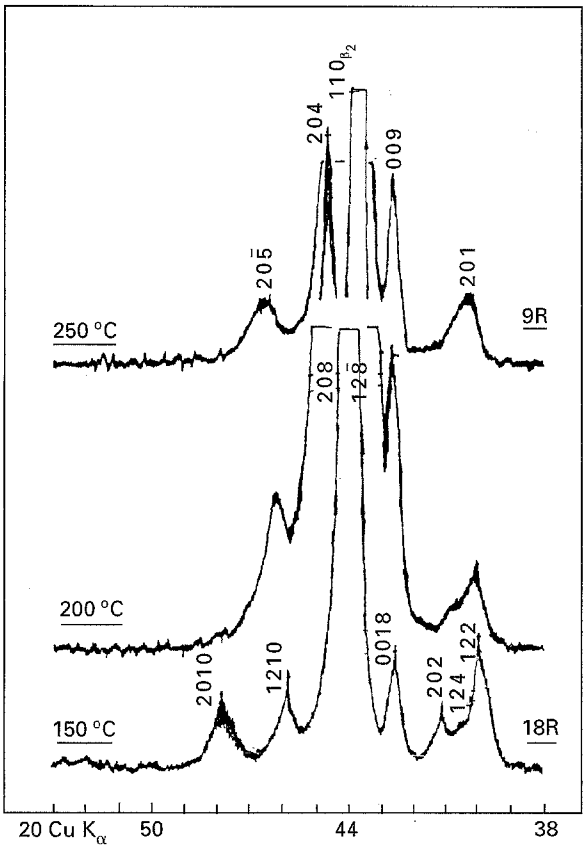

Figure 6 Parts of X-ray diffraction patterns obtained for samples annealed in the temperature range 150–250 °C for 1 h.

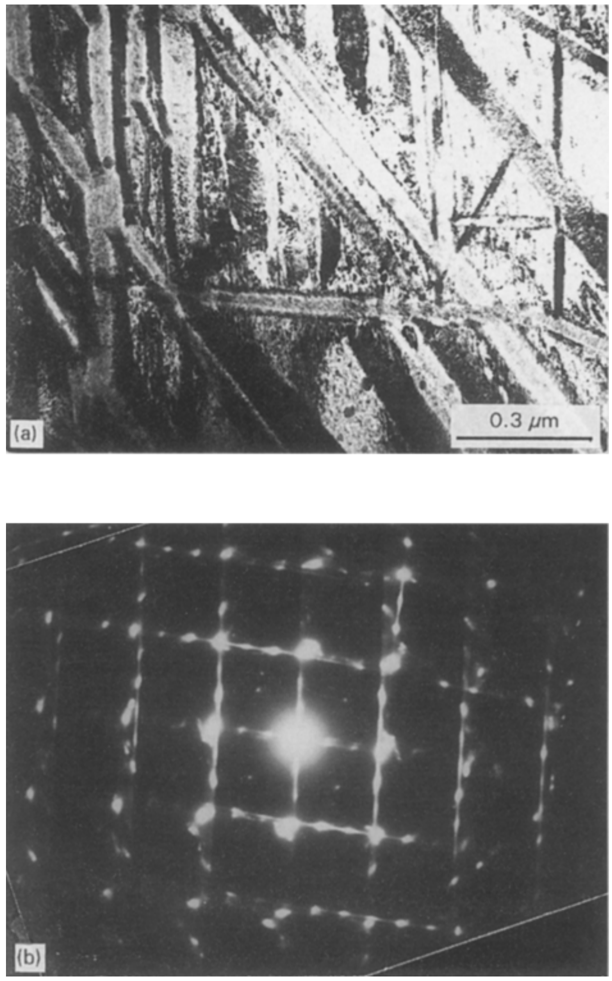

Figure 7 Bainite plates in the matrix phase after ageing at 200 °C for 1 h: (a) image in the bright field; (b) electron diffraction pattern of orientation $\langle 0\,1\,0\rangle_{9R}//[1\,0\,0]_{\beta 2}$.

Investigations were also made of influence of ageing time on structure stability and shape memory characteristic parameters. For this purpose alloy previously quenched from 800 °C in ice water was subjected to ageing at temperature 100 °C for times ranging from 5 min to 300 h. Test results are given in Figs 8 and 9. Ageing, after an initial drop in characteristic temperatures for very short ageing times, leads to a rise in characteristic temperatures. Following ageing of the alloy for a time of more than 100 h a drop in these temperatures is again noted. The one- and two-way shape memory effects behave differently. Ageing of the alloy leads initially to increase and next to gradual lowering of the degree of two-way shape memory effect, while the degree of the one-way effect does not exhibit any appreciable changes throughout the whole ageing range. The reasons for these changes may be seen in the process of NiAl phase precipitation. After ageing for 5 h, a substantial growth in size of these particles is observed on the thin foils (Fig. 10). Negative effects of the ageing process may be noted after 300 h in the form of a repeated lowering of martensitic transformation characteristic temperatures. After this ageing time the alloy structure changes to bainite (Fig. 10(b)).

From analysis of the collected data it may be concluded that with increasing ageing time values of characteristic temperatures increase continuously, particularly rapidly for short ageing times. Bearing in mind the fact that the presence of coherent NiAl particles was ascertained in the aged alloy, it was assumed that they can exert a significant influence on the course of variations of these temperatures. Hence it was taken that increment in characteristic temperatures as a function of ageing time is expressed by the equation

$$\Delta T = At^n$$

TABLE II Influence of annealing temperature on alloy properties (annealing time 1 h)

Temperature (°C)	η (%)	R_m (MPa)	A_{50} (%)	M_s (°C)	M_f (°C)	A_s (°C)	A_f (°C)	$M_s - M_f$ (°C)	$A_f - A_s$ (°C)
	95	711	2.4	50.9	19.6	42.2	65.2	31.3	23
50	91	–	–	53.3	32.9	54.5	68.2	20.4	13.7
100	94	729	2	53	22.5	47	62	29.2	15
150	94	–	–	50	36	51.9	62.8	14	10.9
200	–	946	0.4	–	–	–	–	–	–

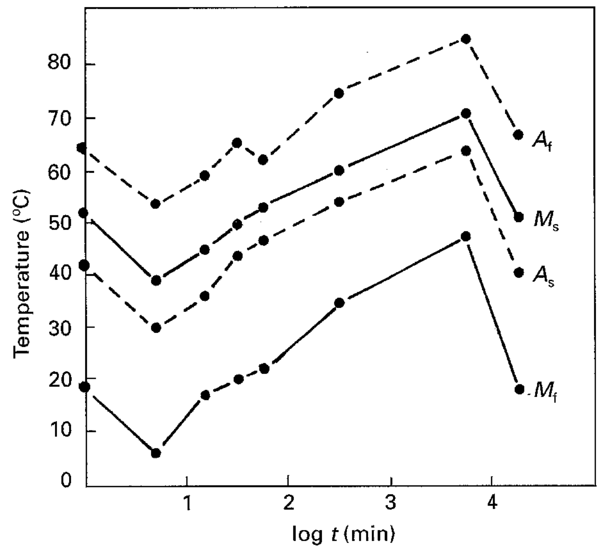

Figure 8 Influence of ageing time at 100 °C on the characteristic temperature of martensitic transformation.

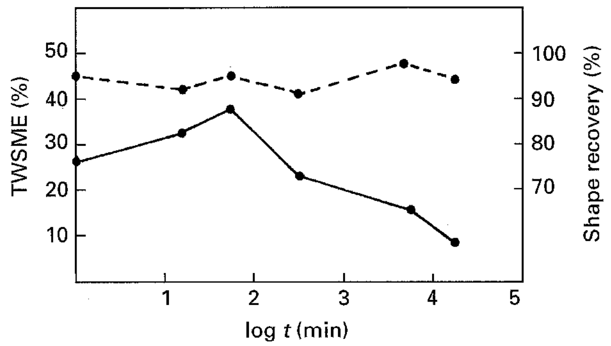

Figure 9 Influence of ageing time on one- and two-way shape memory effect.

After taking the logarithm and fitting by the method of least squares straight lines were obtained as shown on Fig. 11 for which the slope coefficients, for ageing times up to 100 h, had values $n = 0.5 \pm 0.03$ while fitting coefficients lay in the interval from 0.13 to 0.2. For longer ageing times, however, the slope coefficients take negative values.

4. Discussion

The behaviour of the Cu–25.35 wt % Zn–3.87 wt % Al–2.2 wt % Ni alloy, depending on the heat treatment conditions, is influenced by the different processes taking place in it, among which there must be considered processes associated with stabilization of the martensite and also the precipitation of α and NiAl equilibrium phases. Lowering of characteristic temperatures after quenching from lower temperatures is the result of the presence of α-phase in the alloy structure. Increase in quantity of α-phase leads to increase in content of alloy elements in the matrix. According to the propositions of Lee and Wayman [13], Ahlers [14] and Mwamba and Delaey [15], change in M_s temperature is linearly dependent on the

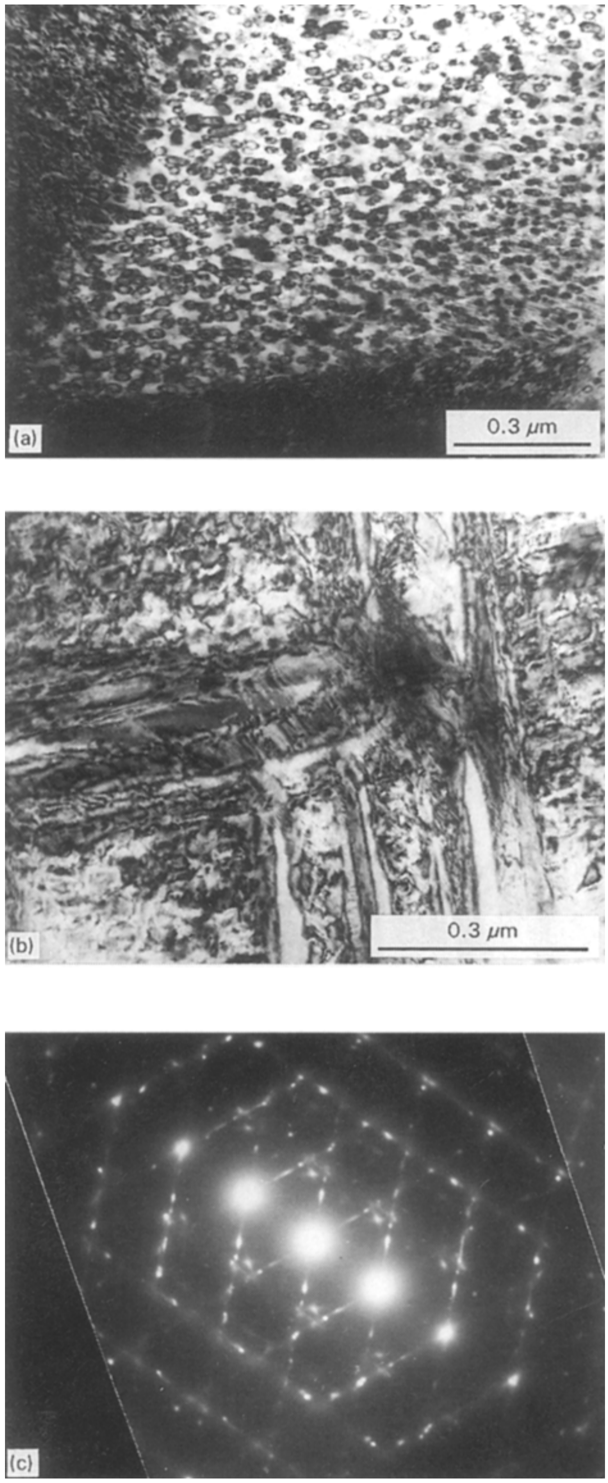

Figure 10 Alloy structure after ageing at 100 °C for 5 h (a) and 300 h (b,c); (c) electron diffraction pattern from twinned bainite plates.

concentration of these elements [15]

$$M_s(°C) = 2481.5 - 66.9\,\text{at}\,\%\,\text{Zn} - 90.65\,\text{at}\,\%\,\text{Al} - 26.73\,\text{at}\,\%\,\text{Ni}$$

The presence of α-phase causes widening of the reversible martensitic transformation hysteresis loop. It also causes a reduction in degree of shape recovery proportional to content of this phase in the alloy, making the assumption that maximum degree of shape recovery is achieved when 100% of the thermoelastic martensite

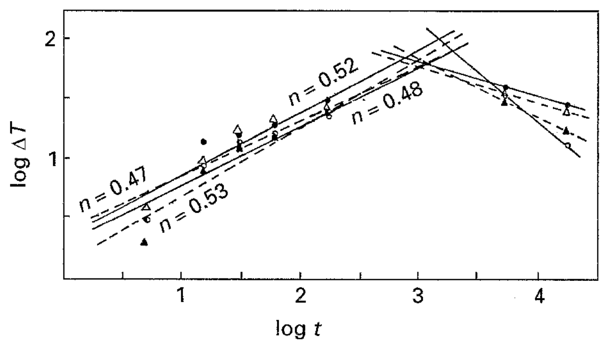

Figure 11 Changes in characteristic temperatures ΔM_s (○), ΔM_f (●), ΔA_s (△), ΔA_f (▲) in a logarithmic scale.

takes part in the reverse transformation. This is confirmed by the data presented in [16]. These observed changes are also induced, though to a considerably smaller degree, by the presence in the martensite of dispersion particles of NiAl. The ease of NiAl phase precipitation made it necessary to investigate the influence of ageing conditions on that process.

Three stages can be distinguished in the kinetics of changes observed during ageing. In the first stage a drop in characteristic temperatures takes place. Similar lowering of characteristic temperatures during ageing of CuZnAl alloys, with stabilized martensite, was reported by Schofield and Miodownik [17] and also by Cook and Brown [18]. According to [19] ageing of these alloys in the temperature range 70–120 °C is not a simple process and may involve a series of effects. The observed drop in temperatures is considerable despite the precipitation of disperse particles of the second phase during cooling.

In the second stage a rise in all the characteristic temperatures is noted while analysis of these changes shows that they are of diffusion type and are associated with further precipitation of coherent particles of NiAl. Hence these changes can be described by the relation $\Delta T = At^{0.5}$.

In the third stage, in which lowering of the characteristic temperatures again takes place, two processes are superimposed i.e. growth in particle size due to which they lose their coherence and development in the process of matrix phase transformation to bainite. It has been shown [20, 21] that the plates of the forming bainite can contain about 3 wt % Zn and 0.5 to 1 wt % Al less than the matrix which in conjuction with the precipitation process causes an appreciable drop in characteristic temperatures. The changes taking place in alloy structure exert a differentiated influence on the shape memory effect. The process of NiAl particles precipitation and next the start of the bainite transformation do not, in principle, influence the one-way shape memory effect (Fig. 9). This one-way shape memory effect disappears at 200 °C when the structure is completely bainitic. It may be seen that the minor quantities of bainite formed at low temperature do not reduce the magnitude of the one-way shape memory effect, especially since in the initial stage of the bainite transformation, the bainite and martensite have the same crystallographic nature [22]. It is under the influence of diffusion at a higher temperature that the bainite plates change their 9R structure to disordered structure [19]. Ageing influences the behaviour of the two-way shape memory effect in a different manner. In the initial stage (up to 1 h) a considerable increase in degree of effect induced is noted, while after longer ageing times (up to 100 h) the precipitation process reduces its magnitude. Then the formation of the bainite structure inhibits the induction of the two-way shape memory effect. This shows clearly that the two-way shape memory effect is more sensitive to the observed structural changes than the one-way effect. The causes of this are to be found in the mechanism of inducing the two-way effect.

5. Conclusions

1. The addition of 2.2 wt % of nickel in a CuZnAl alloy causes precipitation of NiAl disperse particles during quenching and ageing as a result of which the characteristic temperatures of the martensitic transformation are raised. This nickel content may be considered as too high, since it increases the thermal instability of the alloy due to over-rapid precipitation of NiAl particles. Nevertheless, at the same time the precipitation process offers the opportunity for easy control of shape recovery temperature by varying quenching temperature and also ageing temperature and time.
2. Magnitude of the two-way shape memory effect is markedly dependent on degree of advance of the precipitation process and on the start of transformation of the matrix phase to bainite.
3. Modification of the hypoeutectoid CuZnAlNi alloy with titanium and boron made it possible to achieve a fine-grained structure exhibiting high strength properties after quenching, and plastic properties after cooling from the $\alpha + \beta$ two-phase region.

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