Two-Way Shape Memory Effect Induced by Tension Training in Cu-13.4Al-4.0Ni (mass%) Alloy Single Crystals

H. Kato[†], R. Stalmans and J. Van Humbeeck

Department of Materials Science, K. U. Leuven, De Croylaan 2, Heverlee, Belgium

The two-way shape memory effect in CuAlNi shape memory alloy single crystals was studied. The effect was induced by cyclic tensile deformations of superelasticity and shape memory effect, and the efficiency of both methods was examined. Compared with the similar training process in the single crystals of CuZnAl alloys, the CuAlNi alloy showed much smaller changes in stress-strain behaviour and in the resulted two-way memory strain. The superelasticity training had no influence on both the stress-strain behaviour and the dilatation change. By shape memory training, the two-way memory strain increased to saturate at 0.90% after 10 cycles. Associated with this change, particular martensite variants increased its fraction and became "reproductive". However, they were not the variants that were induced during the training, and further increase in the two-way memory strain was impossible by the formation of the observed variants. It was concluded that the present training methods were not effective for the two-way memory effect in CuAlNi shape memory alloy.

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I. Introduction

The term, *two-way memory effect*, refers to the state in which a shape memory alloy remembers its shape in the martensite⁽¹⁾. The alloy can show reversible shape change from a high temperature, the parent phase, shape to low temperature, martensite, shape during thermal cycling through martensitic transformation temperature⁽¹⁾⁻⁽³⁾.

The martensite shape is given by the configuration of martensite variants. In order to remember the martensite shape, it is required to introduce internal stress field leading to the variant configuration for desired shape. The process can be achieved by leaving certain deformation structure after the deformation into the desired shape⁽⁴⁾⁽⁵⁾.

Shape memory effect and superelasticity, although they are essentially reversible deformation, can generate certain deformation structure by repeating it for several times⁽⁶⁾⁻⁽¹⁰⁾. The repetition is one of the effective method to induce two-way shape memory effect⁽¹¹⁾, and is called *training*. The accumulation of deformation structures causes gradual change in the martensitic transformation behaviour. Bands having high dislocation density have been commonly observed after the training. The band appears to be similar to the microstructure observed after several transformation cycles without applied stress⁽¹²⁾⁻⁽¹⁴⁾. Thus, the formation mechanism of the microstructure might be essentially associated with the formation and reversion of martensite.

The defects produced by the uniaxial tensile or compressive stress will have uniform distribution along the

tensile axis. While, by bending or twisting deformation the stress and strain distribution within sample might not be uniform but have gradient. As long as deformation structure has been built up to have internal stress field with such gradient, bending and twisting two-way memory effect can occur⁽⁴⁾. Since the two-way memory effect or the reversible shape change has been frequently observed in bending or twisting shape change⁽¹⁾⁻⁽⁵⁾, the non-uniform distribution of defects would act as the effective nucleation site for the desired martensite variant⁽⁴⁾⁻⁽¹¹⁾.

On the other hand, the two-way memory effect induced by uniaxial deformation has not been intensively studied until recently⁽⁸⁾⁽¹⁰⁾⁽¹⁵⁾⁻⁽¹⁹⁾. In CuZnAl polycrystals the two-way memory strain was below 1.3%⁽¹⁶⁾. While in single crystals of CuZnAl much larger strain of 6.6% has been induced by the repetition of superelasticity in compression, but this is not the case for tension training⁽¹⁵⁾. Later it is found that γ precipitate has been required for CuZnAl alloys to get such a large two-way memory strain⁽¹⁹⁾. The origin for the difference between the two cases seems to be still uncertain at present, although similar dislocation structure has been observed in both cases⁽¹⁵⁾⁽¹⁹⁾.

Two-way memory effect induced by tension training in a CuAlNi single crystal will be described in the present paper. The alloy is a promising candidate for high temperature shape memory alloy. However, the study on the two-way memory effect in the alloy has been lesser known than in CuZnAl alloy. Sakamoto *et al.* have confirmed the appearance by bending training in Cu-13.7Al-3.7Ni (mass%) single crystal⁽²⁰⁾. Although the essential mechanism for the appearance of two-way memory effect may be universal among various copper-based shape memory alloys, the plastic deformation during

[†] On leave from Department of Engineering Physics and Mechanics, Faculty of Engineering, Kyoto University, Kyoto 606-8501, Japan.

cyclic deformation is quite difficult in CuAlNi alloy⁽²¹⁾ so that the deformation structure and the resulting training effect will appear different.

II. Experimental

The CuAlNi single crystals with a rod-shape was grown by the Stepanov method. The nominal composition was 82.6%Cu, 13.4%Al, and 4.0%Ni in mass% (Cu-26.6Al-3.9Ni in atomic percent). The rod-axis of the samples in the parent β_1 phase was close to [001] direction. The material, 3 mm in diameter and 200 mm in length, was cut by slitting wheel and ground by abrasive papers to make two parallel flat surfaces for optical microscopic observation. The samples were solution-treated in air at 1250 K for 3 h, and were quenched in water at R.T.

Samples with a disk shape of $\phi 3 \text{ mm} \times 0.5 \text{ mm}$ were used for DSC measurement with a Du Pont 910 DSC apparatus. The martensitic transformation temperatures, M_s , M_f , A_s , A_f , were measured from the transformation peaks recorded by the DSC. The temperatures measured in different 8 as-quenched samples were different, but existed within $\pm 6 \text{ K}$. The average values of these samples were, $M_s = 375 \text{ K}$, $M_f = 360 \text{ K}$, $A_s = 382 \text{ K}$ and $A_f = 389 \text{ K}$. Tensile test was performed by a INSTRON 1196 machine at a strain rate of $8.3 \times 10^{-5} \text{ s}^{-1}$. Elongation was measured with an extensometer mounted to the center of the specimen's gauge.

The dilatation change during heating and cooling through the martensitic transformation temperature was measured with a linear variable differential transformer connected with both ends of the sample by quartz rods. Compression force was applied by plate springs in order to attach the quartz rod to the sample's end surface. The force can be adjusted from zero to 1.10 N.

The general training routine for shape memory cycling consisted of the following sequence; (1) fixing a specimen to the grips of the tensile testing machine, tensile deformation by 12% strain at R.T., and unloading, (2) removing the specimen from the testing machine, heating it to 453 K on a hot plate, and cooling to R.T. Superelastic training was made by the repetition of stretching a specimen to 8.5% strain and releasing the stress at 420 K, which is above the A_f by about 30 K.

III. Results and Discussion

1. Parameters for shape memory/superelasticity training

(1) Martensitic transformation and related deformation behaviour

According to the result by Stalmans *et al.*^{(16)–(18)}, the two-way memory strain increases linearly with increasing training strain. As the first step, the stress-strain behaviour at different temperatures was examined in order to obtain good efficiency in the training for the two-way shape memory effect.

Fig. 1 Stress-strain curves of a Cu-13.4Al-4.0Ni (mass%) alloy single crystal oriented for [001]. The deformation temperature in Curve (a), 295 K, is lower than the M_f by 70 K, and in Curve (b), 420 K, is higher than the A_f by 31 K.

Stress-strain curves at 295 and 420 K in the as-quenched specimen are shown in Fig. 1. The M_f and A_f is 365 and 394 K so that the specimen before the deformation was fully transformed to martensite in Curve (a) and the parent phase in Curve (b), respectively. In Curve (a) the strain of the first stage was left after unloading, and showed the shape memory effect by heating to 453 K. In Curve (b) two independent superelastic stages can be distinguished. The superelastic strain of the first stage was almost equal to the first stage strain in Curve (a).

The stress of the plateau changed with the deformation temperature, and the relationship is shown in Fig. 2. The open and closed circles are the stress for the forward and the reverse deformation in the first stage, respectively, and the open and closed triangles are those in the second stage. The stress for the first stage changed linearly with temperature, and the extrapolation of the line to the abscissa almost coincide with the M_s temperature. By comparing the stress-strain behaviour and the diagram with those in previous studies^{(22)–(24)}, the first stage in Curve (b) might be the stress-induced martensitic transformation from the parent phase to the β_1' (18R) martensite, and the second might be the transformation from the β_1' to the α_1' (3R) martensite. Then the initial serrated region in Curve (a) is due to the deformation of the thermally-induced β_1' , and the succeeding superelastic stage in Curve (a) is the same transformation as the second stage in Curve (b). The present study will account for the training effect associated with the β_1' martensite⁽²⁰⁾.

Fig. 2 The critical stress vs. temperature relationship in a Cu-13.4Al-4.0Ni (mass%) single crystal before shape memory/superelastic training. The open and closed circles indicate the stress for the forward and reverse deformation of the first superelastic stage observed above the A_f . The triangles are those of the second superelastic stage.

(2) Stabilization of martensite by deformation

The strain left after the deformation at R.T. was recovered by the shape memory effect. It should be noted that the shape recovery did not occur by heating the sample just above the A_f temperature, but it required overheating. Figure 3 shows the DSC curves of the specimen deformed at R.T. similarly as Curve (a) in Fig. 1. The upper curves were obtained in the first heating and cooling runs just after the deformation, where the heating started at Point S. Around 380 K, the A_s , only a small endothermic peak was observed. Instead, reverse transformation with an abrupt and large endothermic peak occurred at 434 K. The DSC curve of the succeeding heating had only one exothermic peak between the normal A_s and A_f temperatures. The curve in the succeeding cycles went through almost the identical path with the second run.

A similar phenomenon has been reported by Quingfu *et al.* on account of the residual martensite after the shape memory cycling under constant load⁽²⁵⁾. The present study shows that the stabilization could be induced not only by the cyclic deformation but also by the monotonous tensile deformation.

Residual martensite has been considered as one of the candidates for the origin of two-way memory effect⁽¹¹⁾. However, it has been also pointed that the magnitude of the residual tensile strain itself have no relation to the increase of two-way memory strain⁽¹⁶⁾, and the accumulation of residual martensite decrease training strain, thus it should degrade the efficiency of the training⁽²⁵⁾⁽²⁶⁾. In the present case the stabilized martensite can be removed by

Fig. 3 The differential scanning calorimeter, DSC, curves measured after 10% tensile deformation at R.T. Exothermic reaction during the forward transformation is exhibited as the peak with positive heat flow. The measurement started by heating from Point S in the upper figure. The lower curve is in the succeeding transformation cycle.

overheating, so the effect was eliminated. In order to avoid the possible aging effect in this alloy⁽²⁶⁾⁻⁽³¹⁾, the sample cannot be heated above 473 K. The A_f temperature of the stabilized martensite was always below 453 K. Therefore, the upper limit of the overheating temperature was limited to 453 K.

2. Effect of training on stress-strain and martensitic transformation behaviour

(1) Effect of training by shape memory cycling

The stress-strain curves before and after the shape memory training are shown in Fig. 4. The two curves have almost identical shape, but the initial length of the specimen before the tensile test was elongated by 1.0% after the training. The difference would consist of two components. One is the plastic strain, which was accumulated during the training. The other is the difference in the dilatation change during martensitic transformation.

Figure 5 shows the DSC curves in the samples without training and after the training of 20 times. The peak position shifted to the lower temperature by the training. It was not altered by the succeeding transformation cycles without load. The change in the M_s and A_f as a function of the training number is shown in Fig. 6. The transformation temperatures became lower as increasing the number. Both temperatures changed by the same amount, so that the hysteresis between the forward and the reverse transformation was almost constant.

The latent heat measured from the peak area in the DSC curve decreased after the training. If we assume that

Fig. 4 Stress-strain curves in a Cu-13.4Al-4Ni (mass%) alloy single crystal deformed at R.T. before and after the shape memory training. In the first deformation, $N=1$, strain was left after unloading by 7.8%. The curve after the 30 training cycles, $N=30$, is drawn such that the unloading point coincides with that of the first cycle.

Fig. 5 The DSC curves of the samples before and after shape memory training. The hatched peaks belong to the curve after 20 shape memory cycles.

the transformation entropy change per unit weight s remains constant, the latent heat of transformation h should change in proportion to the transformation temperature T_c , since $h = sT_c$. As shown in Fig. 7, the slope of the h vs. T_c relationship was almost constant, where h is the average of between heating and cooling transformations, and $T_c = (A_s + M_s)/2$. The constant transformation entropy might indicate that the volume fraction of martensite transformed from the parent phase did not decrease by the training.

In order to determine two-way memory strain, dilatometric change during martensitic transformation was measured along the tensile axis. Accounting for its definition⁽¹⁶⁾, the two-way memory strain in the present case is the spontaneous elongation during cooling transformation, and was measured as shown in Fig. 8. It should be noted that the dilatation change was very sensitive to the compressive stress externally applied along the direction

Fig. 6 The change in the M_s and the A_f temperatures measured by DSC with the number of shape memory training cycles.

Fig. 7 The relationship between the transformation heat and the transformation temperature measured by DSC. The slope of the line gives the entropy change during the transformation, $5.80 \times 10^{-5} \text{ J/kg} \cdot \text{K}$.

of measurement. The spontaneous elongation was suppressed from 0.63% to 0.46% by increasing the compressive stress from 0.05 to 0.22 MPa, as shown in Fig. 8. In the present study we tried to adjust the stress below 0.05 MPa.

Figure 9 shows the dilatation change in a specimen before and after the 20 training cycles. Two-way memory strain of 0.46% appeared before the training, and the strain increased by the training. The development of the dilatation change by the number of shape memory training is shown in Fig. 10. The increase was rapid below 10 cycles, and after 10 cycles it almost saturated at 0.90%.

Fig. 8 Change in the dilatation curve during forward transformation with the compression load applied during the measurement. The two-way memory strain was measured as the difference in length between the parent and martensite phase at the M_s temperature.

Fig. 9 The dilatation curves during heating and cooling through the martensitic transformation temperature. The hatched hysteresis of the dilatation curves is after the 20 shape memory training cycles.

(2) Effect of training by superelastic cycles

The alloy showed superelasticity at 420 K with the transformation strain of 8.6%. Training was made by repeating the superelasticity at the temperature. The stress-strain curves of the first and the 500th superelastic cycles are shown in Fig. 11. Except for the decrease in the flow stress due to the stress-induced transformation, 7 MPa, and the accumulation of the plastic strain by 0.2%,

Fig. 10 Change in the two-way memory strain with the number of the shape memory training.

Fig. 11 Stress-strain curves in a Cu-13.4Al-4Ni (mass%) alloy single crystal deformed at 430 K. The curve drawn by solid and dotted line is the stress-strain curve for the first and after 500 cycles, respectively.

the stress-strain behaviour did not essentially change until it fractured at the 717th cycle in a brittle manner. This is consistent with the results by Sakamoto⁽²¹⁾. Dilatometric measurement showed that the two-way memory strain in the sample after 500 cycles was $0.43\% \pm 0.10\%$, which is the same magnitude before the training. As a result, the superelastic training had no effect for the two-way shape memory effect.

3. Metallographic examination

Figure 12 shows the optical micrographs showing the surface relief of the martensite⁽³²⁾ in the specimens after the shape memory training. Just after the training the top surfaces of these samples were mechanically polished at R.T., which is below the M_f , and heated above the A_f without applied stress and then cooled to R.T. The orientation of the surfaces are different from specimen to speci-

Fig. 12 The surface relief of the martensite after the shape memory training.

men, but the longitudinal directions of all specimens are $[001]$, which is the tensile axis. Then, the (110) and $(\bar{1}10)$ plate groups, which have the twinning plane traces parallel to the $[001]$ direction^{(33)–(35)}, can be distinguished from the other four plate groups, (011) , $(0\bar{1}1)$, (101) , and $(\bar{1}01)$.

In Fig. 13 the fraction of the area occupied by the (110) and $(\bar{1}10)$ plate groups, distinguished by white area in the upper drawing, is plotted as a function of the number of shape memory training. The fraction of area are not necessarily equal to the volume fraction, but might be nearly proportional to it, because the thickness of the polished sample, 0.5 mm, was smaller than the domain size. The fraction of the plate groups (110) and $(\bar{1}10)$ increased by the training similarly with the two-way memory strain shown in Fig. 10.

Since the top surface was polished to be flat in the martensite state just after the training and then the martensite was re-formed, if the martensite variant different from that existing just after the training appeared again, the relief for both variants should be observed overlapping. On the other hand, if the same variant emerges at the same place, the corresponding surface area will remain flat. Here, we will call such martensite variants to be “reproductive.”

Figure 14 shows the optical micrographs of the variants in the (110) and $(\bar{1}10)$ plate groups before and after the shape memory training. In the sample before the training, different configuration of martensite plate groups appeared by the repetition of transformation.

Fig. 13 The fraction of area occupied by the martensite variant in the (110) or $(\bar{1}10)$ plate group. The area is shown by the white region in the upper drawing. The dark area is the domain of the other plate groups, (011) , $(0\bar{1}1)$, $(\bar{1}01)$ or (101) .

Fig. 14 Optical micrographs showing the surface relief of the martensite variants in the plate group, (110) or $(\bar{1}\bar{1}0)$. The photographs of (b), (c) and (d) were taken after the shape memory training for 5, 20 and 50 times.

Thus, overlapping of the relief in the same plate groups, shown in Fig. 14(a), was scarcely observed. Compared with the coarse martensite bands before training, the martensite bands after training became much finer, as shown in Fig. 14(b), (c), (d). Furthermore, several bands with the flat surface, elongated parallel to the variant, increased its width with increasing the number of training. Since these bands have flat surface, the martensite variants were reproductive inside the bands.

4. Two-way shape memory strain

In an ideal state of self-accommodation configuration, all the 24 martensite variants should exist by the same amount to cancel out the anisotropic shape strain of the martensitic phase change^{(33)–(36)}. From the calculation based on the invariant plane theory⁽³⁷⁾, described in Appendix, the self-accommodation state in CuAlNi alloy gives an isotropic contraction of 0.097% during martensitic transformation. However, in the present study the elongation of $0.48 \pm 0.08\%$ was always observed before the training so that the domain configuration should not be the ideal self-accommodation state.

The tensile strain along [001] direction due to the for-

mation of the variants in (110) or $(\bar{1}\bar{1}0)$ plate group is calculated as 0.41%. Since the tensile strain above 8% was given in each training cycle, the other variants giving such large elongation along [001] were expected to be preferentially induced as the result of the training. These variants belong to the (101), $(\bar{1}01)$, (011), or $(0\bar{1}1)$ plate group. Surface observation showed that the domains occupied by these variants decreased their fraction as the training proceeded. The present authors cannot give a conclusive explanation for the above two facts. The analysis for the latter should require the examination of the dislocation structure, or residual martensite, generated by the training, however the present study did not treat the problem.

By comparing the present result for the CuAlNi alloy with a larger amount of studies on this subject in the CuZnAl alloy, a remarkable difference exists in the higher stability of stress-strain behaviour against cyclic deformation in CuAlNi⁽⁶⁾⁽²¹⁾ than in CuZnAl⁽⁸⁾. When superelasticity was repeated several times in the CuZnAl alloy, the decrease in the critical stress for superelasticity⁽⁸⁾⁽¹⁰⁾⁽¹⁵⁾⁽¹⁹⁾ has been observed before exhibiting a large two-way memory strain⁽¹⁵⁾⁽¹⁹⁾. The decrease in the critical

stress is equivalent to the increase of the M_s temperature, which has been indeed observed in CuZnAl alloys⁽⁷⁾⁽¹³⁾⁽²⁶⁾. In the present study the opposite change was observed. While the critical stress decreased but the amount was much smaller than the CuZnAl alloy.

As it has been discussed in Ref. (16), the changes appearing after training, such as the accumulation of residual tensile strain, the increase in transformation temperature, or the decrease in the transformation stress, themselves should not be necessarily required for the appearance of the two-way memory effect, but they might be certain concomitant effects. In CuZnAl alloys the formation of dislocation tangles followed by the development of the bands with high dislocation density has been observed⁽⁸⁾⁽¹⁰⁾. Such a deformation structure could not be generated by the present training method in the CuAlNi alloy. It might be the reason why the tension training did not induce an appreciable two-way memory strain in the present study.

IV. Concluding Remarks

When a Cu-13.4%Al-4%Ni (mass%) alloy single crystal with the [001] tensile axis suffered the training by the shape memory effect, the transformation temperature decreased and the two-way memory strain increased. The maximum two-way memory strain was 0.90%, which saturated after 10 cycles. While superelasticity training caused no appreciable change in the martensitic transformation and stress-strain behaviour until brittle fracture at 717 cycles, and the two-way memory effect was not improved.

Although both two training methods included the process to induce the variants of the β'_1 martensite which can show 8% strain along the tensile axis of [001], the variants were not induced in the martensitic transformations after the training. Instead, the variants of the other plate groups, (110) or ($\bar{1}10$), which have 0.4% tensile strain, increased its fraction. Inside the plate-groups the region where these martensite variants were "reproductive" grew its width by the shape memory training.

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Appendix

Shape change of a unit cell in the parent phase to the corresponding martensite cell is known from the lattice correspondence, the Bain strain, and the orientation relationship between the cells⁽³⁷⁾. The shape change calculated for the invariant plane condition has been confirmed for its validity in many crystallographic aspects of Cu-based shape memory alloys⁽²²⁾⁽³⁵⁾⁻⁽³⁷⁾. Here, the calculation of the magnitude of shape change during the β_1 to β'_1 transformation has been done by the similar manner to the case of CuZnGa alloys by Saburi *et al.*⁽³⁶⁾, using the lattice parameters of the Cu-14.2Al-4.3Ni (mass%)⁽²²⁾. The shape change of a unit cell can be represented as,

$$\begin{pmatrix} 1.07888 & 0.07548 & -0.01712 \\ -0.08936 & 0.91449 & 0.01938 \\ -0.01712 & -0.01638 & 1.00371 \end{pmatrix}, \quad (1)$$

where the variant is denoted as “4(–)” by the Saburi and Wayman’s notation⁽³⁵⁾. It is the variant that has the basal plane corresponding to the (101) plane in the parent phase, and one of the four variants in the (110) plate-group. When the martensitic transformation occurs, the unit column vector of $\langle 100 \rangle$, $\langle 010 \rangle$ and $\langle 001 \rangle$ in the parent phase is transformed to the vector of the first, the second, and the third column of the matrix, respectively. These unit vectors change its length by 8.27%, –8.23%, and 0.40%. It means that 8.27% strain is possible for the tensile test along the $\langle 100 \rangle$ and 8.23% for the compression along the $\langle 010 \rangle$ direction. The matrix for the other variant can be obtained by the symmetrical operation, which describes the transformation between different lattice correspondence. All these matrices for the CuZnGa alloys are listed in the paper by Saburi *et al.*⁽³⁶⁾.

The shape change matrix of the following three simple

configuration of variants can be readily obtained. (i) When all the four variants of the (110) plate-group are formed by the same amount, the shape-change matrix has a symmetric form.

$$\begin{pmatrix} 0.99669 & -0.00694 & 0 \\ -0.00694 & 0.99669 & 0 \\ 0 & 0 & 1.00371 \end{pmatrix} \quad (2)$$

Only the $\langle 001 \rangle$ directions does not rotate during the transformation, and elongates by 0.37%. While the $\langle 100 \rangle$ and $\langle 010 \rangle$ should rotate and contract by 0.33%. (ii) When all the eight variant of the (110) and the $(\bar{1}10)$ plate-group are formed together, all the off-diagonal components in eq. (2) vanish. Then all the [001] vectors do not rotate, but the change in length is still anisotropic along the $\langle 001 \rangle$ direction. (iii) For the shape change to be isotropic, all the 24 variants should exist by the same amount. When it occurs, any vector should not change in its direction by the transformation, and the shape deformation is the isotropic contraction of 0.097%.