

Mechanism of two Way Shape Memory Effect Obtained by Stabilised Stress Induced Martensite

J.M. Guilemany and J. Fernández

Metalurgia Física-Ciencia de Materiales, Dept. de Ingeniería Química y Metalurgia, Facultad de Química, Martí i Franquès, 1. E-08028 Barcelona, Spain

Abstract : Two Way Shape Memory Effect (TWSME) involves thermomechanical routines which produce some plastic deformation or complex dislocation arrays during the training procedure. The results of TWSME obtained by these thermomechanical training routines are not as good as would be expected because new dislocations are generated during thermal cycling. These dislocations may interact with those that provide TWSME to the alloy. The present authors have developed a completely new training method which involves the stabilisation of the stress induced martensite (SSIM). The present work has been carried out to improve knowledge of the mechanism of TWSME obtained by the SSIM training method. The results show that the new training method not only improves the values of TWSME but also gives improved stability to this TWSME.

1. INTRODUCTION

In the last three years, different training routines have been developed to give the Two Way Shape Memory Effect (TWSME) all of them based on the repetitivity of a thermomechanical training routine (1-3). These new methods attempt to improve the results of TWSME by conventional training routines which have been extensively used previously (4-7). Each of them is based on the generation of dislocations, during the training procedure, which remain in the material in the subsequent thermal cycles so providing TWSME.

On the other hand, thermal cycling generates new dislocations which interact with those that provide TWSME, which means that there is a reduction in TWSME.

Ni-Ti alloys are trained in a completely different way when compared with the methods used for copper based alloys (8-10). Ni-Ti alloys are trained by constrained ageing between 300° and 500° C for 1 hour. This kind of training process provides not only TWSME but also All-Round Shape Memory Effect (ARSME).

Complex Ni-rich precipitates are formed during ageing these alloys (11) (12). These precipitates produce internal stress fields which control the growth of the martensite variants providing TWSME or ARSME. However, Liu and McCormick (13) and Todoroki et al. (14) have found that the presence of the R phase during the martensitic transformation in Ni-Ti alloys leads to a lower TWSME.

A training process based on the stabilisation of the stress induced martensite (SSIM) has also been developed, in recent years, for Cu-based alloys (15-20). The aim of the present work

is to improve our knowledge of the mechanism of TWSME obtained by SSIM in a polycrystalline Cu-Zn-Al-Co alloy.

2. EXPERIMENTAL METHOD

Two Cu based alloys have been prepared by melting high purity metals in a vacuum sealed quartz tube. The ingot was subsequently homogenised at 850 °C for 12 hours and hot rolled into 0.5 mm thick plates. Alloy compositions in wt % together with the M_s temperature are shown in Table I.

Table I. Alloy compositions and M_s temperatures.

ALLOY	Cu	Zn	Al	Co	M_s (°C)
1	72.5	20.2	6.6	0.7	30
2	73.9	18.9	6.7	0.5	5

Several samples 70 mm long x 5 mm wide x 0.5 mm thick were cut from the sheets and trained by SSIM method, previously described (18-20). Samples taken from alloy 1 have been trained at different temperatures between 50 and 240 °C with an interval of 10 °C. Samples taken from alloy 2 have been trained from 30 to 170 °C with an interval of 20 °C.

Samples which were untrained and trained by treatments at 100, 150 and 200 °C, for alloy 1, and by treatments at 130 and 170 °C, for alloy 2, have been examined by optical and TEM-STEM. For the TEM examination, discs 3 mm in diameter have been prepared by cool ion beam at 4 kV with an initial tilt of 10° and a final tilt of 5°. A TEM-STEM Hitachi H-800-MT equipped with an EDS X Ray microanalysis system have been used (200 kV).

3. RESULTS AND DISCUSSION

Both alloys contain three kinds of Co-rich precipitates before training, as has been previously described (21). The original β phase of alloy 2 before training is shown in Figure 1. Small amount of martensite can be seen near the grain boundaries. This martensite has appeared as a consequence of the nucleation effect that grain boundaries have, in locally raising the M_s above room temperature.

Once the samples are trained, eg. $T_{\text{training}} = 150$ °C, they exhibit a large amount of stabilised stress induced martensite, see Figure 2, and subsequently show TWSME. Thus, TWSME could be related with the presence and the amount of the SSIM obtained during training (18) (22).

Similar results have been obtained for alloy 1. But it is not possible to distinguish between the initial martensite and SSIM because the alloy is almost fully martensitic before training. However, samples trained have fewer martensite variants than the untrained ones, meaning that the thermal martensite, which appeared on cooling, has nucleated and grown under the influence of the SSIM.

The structure of alloy 1 trained at 100 °C for 30 minutes is shown in Figure 3. A large quantity of γ precipitates are seen having an average size of 10 - 15 nm. Other samples trained at 150 and 200 °C also have γ precipitates with a size of 15 - 25 nm and 20 - 30 nm, respectively. Trained samples of the alloy 2 also exhibit γ precipitates, Figure 4, with a size of 15 - 20 nm in the case of the sample trained at 170 °C for 30 minutes.

A particular characteristic is that, in all cases, these γ precipitates contain cobalt in their composition (21).

Coherency strain fields were observed after treatment at temperatures up to 170 °C, Figure 5, but after treatment at 200 °C the coherency strain fields were absent.

The matrix is supersaturated with respect to cobalt since the alloy is quenched from 850 °C prior to the training treatment. During the training procedure, the matrix rejects the excess Co in the form of small coherent precipitates.

Hence, the γ precipitates, which also form during training, nucleate heterogeneously on the coherent Co precipitates, although they can also nucleate homogeneously. The first type of nucleation is energetically favoured, thus, most γ precipitates are heterogeneously nucleated and show a central Co rich core.

The process of γ precipitation on coherent cobalt precipitates is accelerated by increasing the training temperature. Thus, with the sample trained at 200 °C, γ has precipitated on almost all the Co particles so that coherency strain fields are no longer visible (21).

De Graef et al. (23) have found small γ precipitates at the martensite plate boundaries after ageing a cobalt free Cu-Zn-Al alloy at 100 °C for 3 days. The difference in time for precipitation may be attributed to the fact that the Co precipitating from the supersaturated matrix accelerates the precipitation of γ by heterogeneous nucleation.

The % of TWSME is directly related to the amount of SSIM as can be seen from Figure 2 and Table II (18). The presence of the stabilised stress induced martensite allows the nucleation and growth of particular martensite variants so providing TWSME.

Table II. % of TWSME for the different training temperatures (°C) during cycling (N) for alloy 2.

N	% TWSME							
	30 °C	50 °C	70 °C	90 °C	110 °C	130 °C	150 °C	170 °C
1	17	30	37	52	68	60	60	61
10	17	32	40	52	68	60	60	61
100	20	32	37	55	65	57	63	61

The precipitation of γ plays an important role because it stabilises the stress induced martensite by local depletion of Al and Zn from the matrix so raising the M_s temperature. At the same time, the precipitates make it difficult for the martensite to retransform. Thus the M_s is raised by mechanical impingement.

4. CONCLUSIONS

1.- The stabilised stress induced martensite provides the two way shape memory effect by promotion of particular martensite variants.

2.- The stabilised stress induced martensite can be obtained by γ precipitation during the training procedure. This precipitation is aided by the presence of Co precipitates formed from the supersaturated matrix.

3.- The γ precipitates deplete the matrix of Al and Zn locally raising the martensitic transformation temperature. They also have an impingement effect which mechanically increases the M_s .

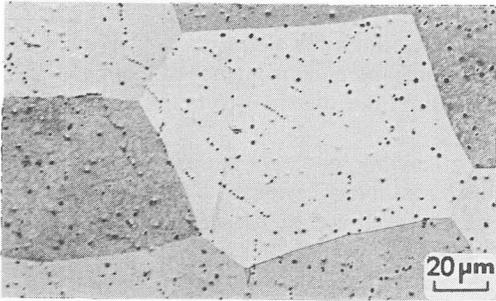


Figure 1. Original β structure of the alloy 2.

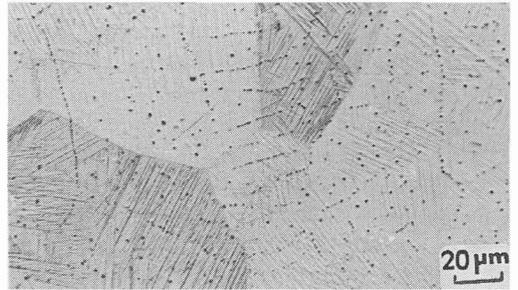


Figure 2. Structure of the sample aged at 150°C (alloy 2) with the presence of SSIM.

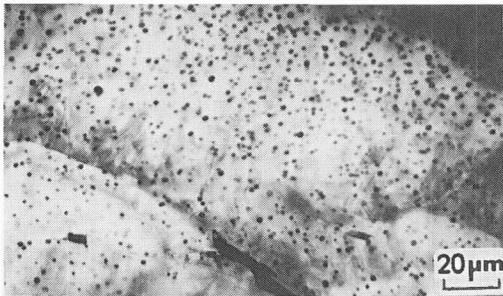


Figure 3. Gamma precipitates present in the trained alloy 1.

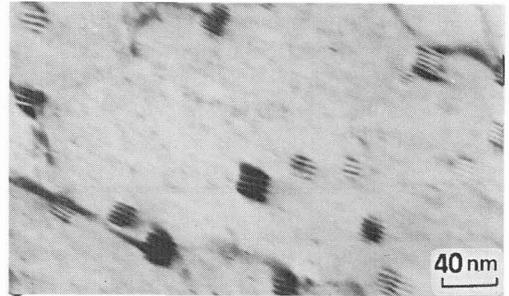


Figure 4. Gamma precipitates found in the trained alloy 2.



Figure 5. Coherency strain fields formed during the training of alloy 2.

5. ACKNOWLEDGEMENTS

The authors acknowledge the CICYT of SPAIN for financial support to carry out this work, under the Project MAT92-1025-CO2-02. They also acknowledge Prof. J. Nutting in sabbatical year in the University of Barcelona (CICYT SAB93-0020) for his careful and critical reading of the paper.

6. REFERENCES

- [1] Flores Zúñiga H., Belkahla S., Guénin G., " The thermal ageing and two way memory effect (TWME) in Cu-Al-Be shape memory alloy ", Martensitic Transf. and Shape Memory properties, Aussois (France), 16-18 September, 1991, pp. 289-294.
- [2] Morris M. A., *Acta Met. et Mater.*, **40**, (1992), pp. 1573-1586.
- [3] Stalmans R., Van Humbeeck J., Delaey L., *Materials Transactions JIM*, **33**, (1992), pp. 289-293.
- [4] Wasilewski R. J., *Scripta Met.*, **9**, (1975), pp. 417-422.
- [5] Schroeder T. A., Wayman C. M., *Scripta Met.*, **11**, (1977), pp. 225-230.
- [6] Perkins J., *Materials Science and Engineering*, **51**, (1981), pp. 181-192.
- [7] Duerig T. W., Albrecht J., Gessinger G. H., *Journal of Metals*, (1982), pp. 14-20.
- [8] Nishida M., Honma T., *Scripta Met.*, **18**, (1984), pp. 1293-1298.
- [9] Nishida M., Honma T., *Journal de Phys., Colloque C4, suppl. au n° 13*, **43**, (1982), pp. 225-230.
- [10] Nishida M., Wayman C. M., *Scripta Metall.*, **18**, (1984), pp. 1389-1394.
- [11] Nishida M., Wayman C. M., " R-phase type transformation of Ti₂O₃ precipitates in aged Ti-52 at% Ni ", Proc. Int. Conf. on Mart. Transformation, ICOMAT'86, Nara (Japan), 1986, pp. 653-658.
- [12] Honma T., " The effect of ageing on the spontaneous shape change and the all-round shape memory effect in Ni-rich TiNi alloy", Proc. Int. Conf. on Mart. Transformation, ICOMAT'86, Nara (Japan), 1986, pp. 585-590.
- [13] Liu Y., McCormick P. G., *Materials Science Forum*, **56-58**, (1990), pp. 585-590.
- [14] Todoroki K., Tamura H., Suzuki Y. " Variable temperature stress-induced martensitic transformation training of Ni-Ti alloy ", Proc. Int. Conf. on Mart. Transformation, ICOMAT'86, Nara (Japan), 1986, pp. 748-753.
- [15] Rapacioli R., Torra V., Cesari E., Guilemany J. M., Miguel J. R., *Scripta Metall.*, **22**, (1988), pp. 261-264.
- [16] Lee I. Ch., Chung I. S., *Scripta Metall.*, **23**, (1989), pp. 161-166.
- [17] Leu S. S., Hu C. T., *Scripta Metall.*, **23**, (1989), pp. 1925-1930.
- [18] Guilemany J. M., Fernández J., Mellor B. G., *Scripta Metall. et Mater.*, **24**, (1990), pp. 1941-1945.
- [19] Guilemany J. M., Mellor B. G., Fernández J., *J. of Materials Science Letters*, **11**, (1992), pp. 964-967.
- [20] Guilemany J. M., Fernández J., *Scripta Metall. et Mater.*, **30**, (1994), pp. 59-61.
- [21] Guilemany J. M., Fernández J., *Scripta Metall. et Mater.*, **30**, (1994), pp. 319-323.
- [22] Guilemany, J. M., Rapacioli R., Miguel J. R., *Inst. Phys. Conf. Ser.*, **2 (13)**, EUREM 88, (1988), pp. 491-492.
- [23] De Graef M., Van Humbeeck J., Dealey L., " TEM observations of stabilised Cu-Zn-Al martensite ", Proc. Int. Conf. on Mart. Transformation, ICOMAT'86, Nara (Japan), 1986, pp. 850-855.