*Association of Metallurgical Engineers of Serbia* *Review paper*
*AMES* *UDC:611.314:669.245'295+669.715'3''24=20*

# MICROSTRUCTURE AND PROPERTIES OF NiTi AND CuAlNi SHAPE MEMORY ALLOYS

A. C. KNEISSL[1], E. UNTERWEGER[1], M. BRUNCKO[1,2], G. LOJEN[2], K. MEHRABI[1], H. SCHERNGELL[3]

*[1]Department Physical Metallurgy and Materials Testing, Montanuniversität Leoben, Austria, [2]Faculty of Mechanical Engineering, University of Maribor, Slovenia, [3] Formerly at the Department Physical Metallurgy and Materials Testing, Montanuniversität Leoben, Austria*

ABSTRACT

This paper deals with NiTi and CuAlNi shape memory alloys and especially with the two-way memory effect which was successfully introduced in wire specimens by a specific thermo-mechanical heat treatment called training. In order to enable a systematic variation of the microstructure with respect to dislocation density, second phase particles and grain size, the investigations were carried out on three different alloy systems. 4000 thermal cycles were performed on the trained shape memory elements, continuously observing the changes in the deformation behavior. The influence of work hardening, grain size and high internal stress-fields on the development and the stability of the intrinsic two-way shape memory effect is discussed, supported by microstructural investigations. It is shown that the stability of the two-way shape memory effect can be optimized by establishing an appropriate microstructure. Furthermore this work deals with the production of thin ribbons of shape memory alloys by melt-spinning and optimization with respect to microstructure and functional properties.

**Key words:** microstructure, shape memory alloys, NiTi, CuAlNi

## INTRODUCTION

Shape memory alloys (SMAs) have been successfully introduced in a variety of technical areas over the past few years. A very promising field for a high-volume application of SMAs in the near future is the actuator technology, since with a shape memory element, a pre-determined response can be obtained very easily by thermal or electric stimulus. Especially the possibility to realize even complicated movements with an element of simple design and compact size makes shape memory actuators very attractive. From the several modes of using the shape memory effect, the intrinsic two-way shape memory effect (TWSME) is the most suitable to apply in actuators since no resetting force has to be considered in design and one can truly choose from a variety of shapes and configurations. However, when dealing with the inherently weak intrinsic two-way shape memory effect, it is essential to elaborate thoroughly the fatigue process. For technical applications it is important to know how changes of the substructure quantitatively and qualitatively affect the magnitude of the effect and possibly the element's dimensions and actuating temperatures.

Since numerous literature on crystallography and thermodynamics of the shape memory effects are available (e.g.[1–4]), in this paper only short phenomenological descriptions are given. Characteristic for shape memory materials is an unconventional, unique correlation of strain, stress and temperature, which is based on crystallographic reversible thermoelastic martensitic transformation. The low-temperature and the high-temperature phases are, analogous to steel technology, named martensite and austenite. The transformation-start and –finish temperatures are $A_S$ (austenite start) and $A_f$ (austenite finish), and $M_S$ (martensite start) and $M_f$ (martensite finish) during heating and cooling, respectively. The temperature-triggered transformation can be accompanied by unusually large strain; if external forces constrain the deformation, the stress can strongly increase (capability to perform mechanical work). At temperatures above $A_f$ but below $M_d$ (the highest possible temperature for the formation of stress-induced martensite), the reversible martensitic transformation can be triggered by an increase of stress level. In this case, an unusually large strain accompanied by very small additional stress increase is possible (pseudoelasticity). When unloaded, transformation and shape change in the reverse direction and order take place. Above $M_d$ plastic transformation would occur before the onset of the martensitic transformation.

When martensite is deformed and then heated to the austenitic state, the material returns to the shape it had before the pseudoplastic deformation. The pseudoplastic deformation is characterized not by gliding and generation of dislocations but rather by the movement of twin boundaries thereby reducing the number of different martensitic variants. Upon subsequent cooling, the shape remains unchanged. This phenomenon is known as one-way shape memory effect since there is a shape change during heating only and not during cooling. It is a natural crystallographic property of shape memory materials (Fig. 1, 2). Strain values up to 8% can be recovered in polycrystalline NiTi alloys.

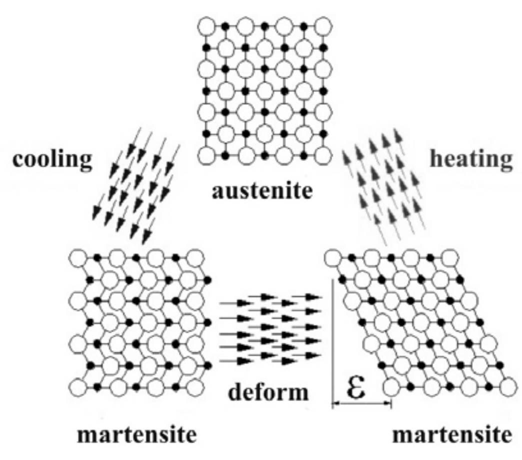


*Fig. 1: The Shape memory effect (atomistic, schematically)*

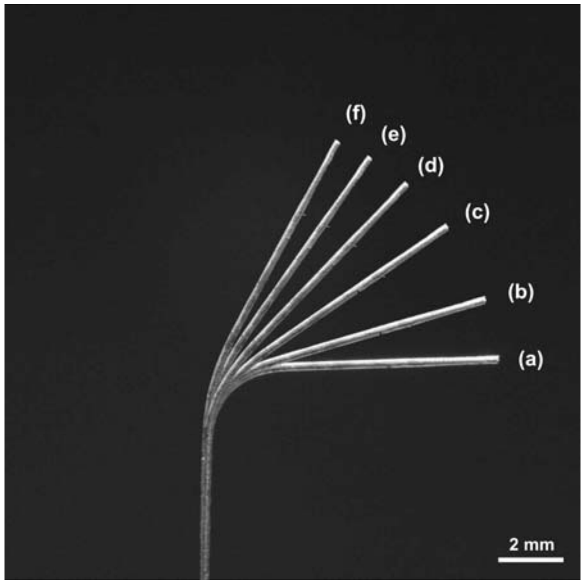


*Fig. 2: Shape change of a NiTi specimen during heating; (a) after deformation and (b – f) various stages of shape recovery during heating*

A natural property of shape memory specimens is to “remember” the shape they had before the pseudoplastic deformation in martensitic state, and not to “remember” the shape given through this deformation. But they can “learn” this by training. Training is a cyclic thermomechanical treatment creating a microstructure and stress fields, which enforce austenite to transform to exactly those martensitic variants (and through this to the same outer shape) that were introduced by previous pseudoplastic deformation in martensitic state. So, TWSME means that the material has one shape in the martensitic state and another one in the austenitic state. The shape changes every time when martensitic transformation takes place in one or the other direction. Reversible strains of the two-way shape memory effect are significantly smaller than of the one-way effect; up to 4% for NiTi alloys and even smaller for Cu-based SMAs.

The most well-known shape memory alloy is NiTi with about equiatomic composition (Fig. 3). The transformation temperatures decrease strongly with increasing Ni content. The high-temperature phase (austenite) has an ordered bcc structure (B2), the low-temperature phase (martensite) has an ordered monoclinic structure (B19’).

Among the Cu-based SMAs, the most frequently applied are CuZnAl and CuAlNi alloys. The latter are indeed more expensive than the former, but among the Cu-based SMAs, they are the most resistant to degradation of functional properties due to undesired aging effects. The most important disadvantage of polycrystalline CuAlNi alloys is the small reversible deformation (one-way shape memory effect: up to 4%; two-way effect: only approximately 1.5%) due to intergranular brake down already at low average stress levels. On the other hand, the CuAlNi alloys are considerably cheaper than NiTi alloys and, in addition, at present they are the only option if high transformation temperatures are required. The characteristic temperatures of martensitic transformation of CuAlNi alloys can lie between -200 and 200°C and depend on Al and Ni content; the influence of Al is much stronger.

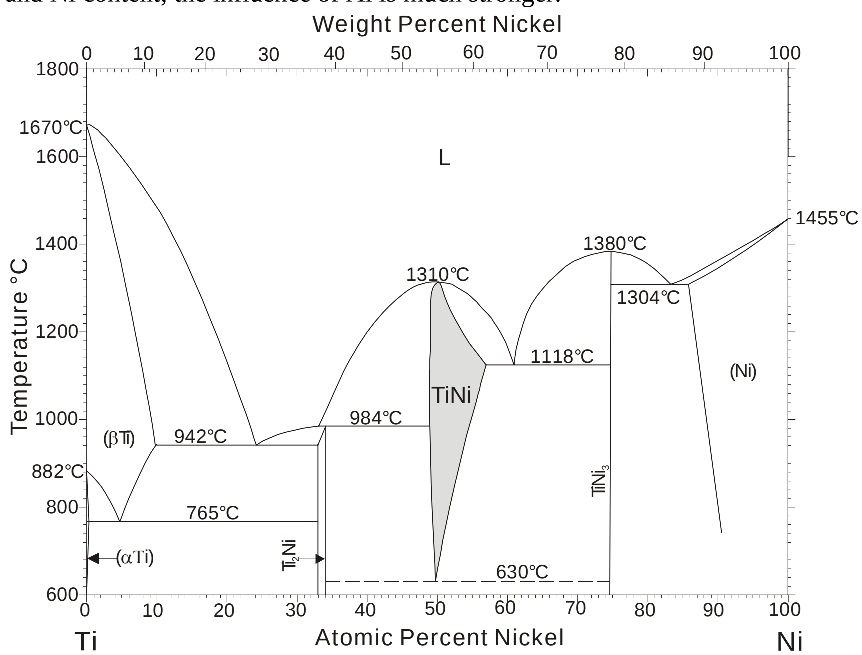


*Fig. 3: Ni-Ti equilibrium diagram [5]*

The shape memory properties of CuAlNi alloys are based on the properties of the high-temperature binary CuAl phase β, having a body centered cubic structure. During cooling, this phase undergoes the eutectoid decomposition $\beta \rightarrow \alpha + \gamma_2$ at 565°C. High cooling rates can prevent the eutectoid decomposition and enable the martensitic transformation. Nickel in ternary alloys efficiently slows down the diffusion of Cu and Al. On cooling, this helps to retain the single-phase condition until the $M_S$ temperature is reached. With increasing Ni content, the brittleness of the alloy increases and the eutectoid point shifts to higher Al contents. Therefore, the optimal chemical composition of CuAlNi SMAs is about 13 wt.% Al and 3 - 4.5 wt.% Ni. In order to ensure the undercooling necessary to enforce the martensitic transformation, in general, a heat treatment cannot be avoided. It consists of annealing in the temperature range of stable β phase and subsequent water quenching (β quenching).

## EXPERIMENTAL

At the beginning, tensile tests have been carried out to investigate the mechanical behaviour of shape memory alloy samples in the martensitic (room temperature) and austenitic (180°C) state (e. g. Fig. 4). For the training experiments three different alloy systems were used: i) binary NiTi indicated as alloy A, which represents a standard SMA; ii) a dual phase alloy B consisting of a NiTi matrix containing dispersoids of tungsten to investigate the influence of second phase particles; iii) a CuAlNi alloy C, which is appropriate to elaborate the influence of grain size and which moreover represents the only commercially available shape memory alloy system, with which transformation temperatures beyond 200°C can be realized. For each alloy the shape of the as-received material consisted of wire material with a diameter of 3 mm. The NiTi-based alloys were hot extruded and reduced to the final diameter by stepwise cold drawing and intermediate annealing. A cold-work of 13% remained in the as-received condition of this material, resulting from the last step of cold drawing. In contrast, the CuAlNi was hot extruded till its final shape due to its poor ductility.

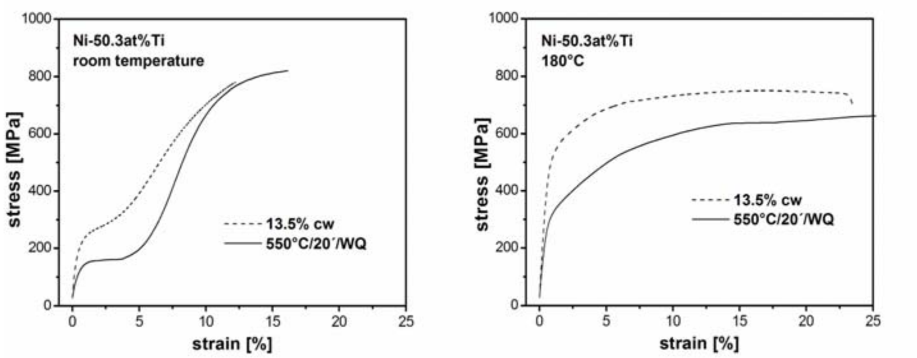


*Fig. 4: Mechanical behaviour of a NiTi alloy in the cold worked ( cw) and annealed condition at room temperature and at 180°C*

This selection of alloys in combination with appropriate heat treatments assured that a wide variation of the initial microstructure with respect to dislocation density, second phase particles and grain size was obtained. The nominal composition of the alloys as well as the heat treatments of the samples are summarized in Table 1. Specimens A2 and B2 of the NiTi-based alloys were annealed at 550°C in order to create a condition with a recovered microstructure in comparison to the cold-worked (cw) as-received conditions A1 and B1. Specimens of alloy C were subjected to a heat treatment in the β-region, a precondition to observe the shape memory in Cu-based alloys. The duration of annealing in the β-region was varied between specimen C1 and C2 in order to establish two different grain sizes in the corresponding microstructures. The $M_f$ temperatures of the NiTi(W) alloys are around 40°C while the corresponding transformation temperatures of the CuAlNi alloys lie around 150°C.

*Table 1: Nominal composition and heat treatment of the investigated samples.*

| Specimen | Nominal composition [at. %] | Heat treatment |
|---|---|---|
| A1 | Ni-50,3Ti | 13,5% cw |
| A2 | Ni-50,3Ti | 550°C/20'/WQ |
| B1 | Ni-50,3Ti-2W | 13,5% cw |
| B2 | Ni-50,3Ti-2W | 550°C/20'/WQ |
| C1 | Cu-25,8Al-3,6Ni | 800°C/90''/WQ |
| | | 300°C/120'/WQ |
| C2 | Cu-25,8Al-3,6Ni | 800°C/120'/WQ |
| | | 300°C/120'/WQ |

A uniaxial two-way shape memory effect has been induced in wire specimens of alloy A to C by a thermomechanical training treatment. The wire specimens were thermally cycled through the temperature range of phase transformation under a constant stress that had been applied at room temperature. Heating was done by direct passage of current, cooling with pressurized air. The change of length during the transformation cycles was measured using ceramic edges for microstrain measurement with a strain gauge. The temperature was controlled by three thermocouples. Length and temperature were continuously recorded. After training, the specimens were unloaded and the shape change upon free thermal cycling – representing the induced intrinsic TWSME - was determined. Afterwards, the TWSME was executed for several thousand times, continuously observing the changes in the deformation behaviour and thereby monitoring the stability of the effect.

Besides the commercial wire material used for the investigations described above, thin ribbons of CuAlNi with almost the same composition as shown in Table 1 have been produced using a melt-spinning method (Fig. 5) in order to miniaturize shape memory elements for possible applications in the field of microsensors and microactuators.

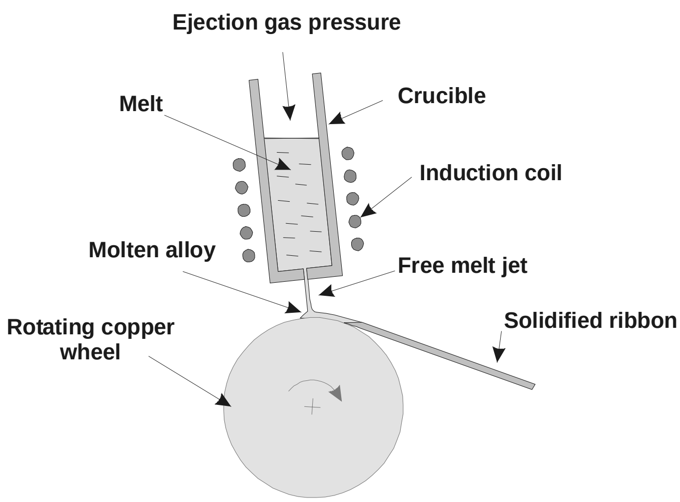


*Fig. 5: Free jet melt-spinner, schematically*

The melt–spinning process starts with induction melting of the alloy in a graphite crucible. As known from the literature [6-8] Cu melts do not show any reaction with graphite and the solubility of graphite also is negligibly low. When an overpressure is applied within the crucible the melt will flow onto a rotating copper wheel. The solidified ribbons are gathered subsequently in a collection tray. The process is carried out under protective gas in the present case.

This process is influenced by several parameters. These are for example the circumferential velocity of the wheel, the overheating of the melt during the casting procedure, the overpressure in the crucible, the shape of the nozzle and its distance from the wheel. Varying these parameters permits to produce ribbons of different geometries. The surface finish, microstructure, and mechanical and functional properties as well, are also dependent on the parameters set. Unfortunately, data of the cooling speed is not available. Some indication of the cooling speed can be derived from the ribbon thickness [9].

## RESULTS AND DISCUSSION

Fig. 6 shows the martensitic microstructure of the NiTiW alloy which can be recognized by the typical surface relief. To visualize the W-dispersoids a surface layer etching was applied (Fig. 7). For training of the wire samples a constant external stress was applied while the specimens were thermally cycled through the transformation range.

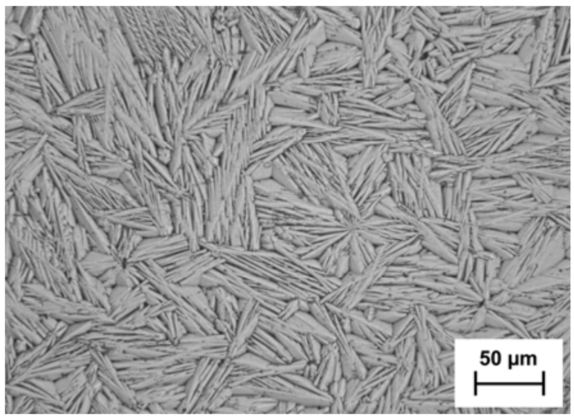


*Fig. 6: The martensitic microstructure of alloy B2*

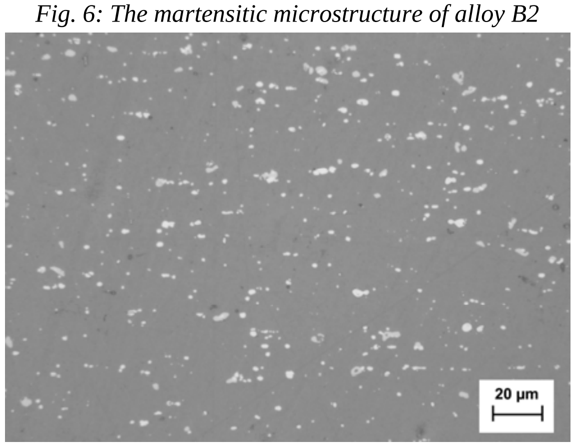


*Fig. 7: W – dispersoids in alloy B2, surface layer etching*

As the forward transformation (during cooling) occurs under external load, the stress field causes a preferred nucleation and growth of those variants that have the highest compatibility with the stress field. Consequently, only a small number of variants is generated and the growth of this oriented martensite results in a macroscopic strain in the direction of the applied stress. Nearly all of this strain is of pseudoplastic nature, thus recovering during heating and restoring the original shape but at each cycle a tiny amount of true plastic (irreversible) strain is induced, thereby building up gradually a microstructure with a certain internal stress field which causes the material to "remember" the low-temperature shape even after removal of the external load (Fig. 8). In this figure the higher strain corresponds to the martensitic state, the lower strain to the austenitic state. The difference is the pseudoplastic strain. The results of the training treatment are summarized in Table 2, $\varepsilon_{2w}$ denoting the size of the two-way shape memory effect.

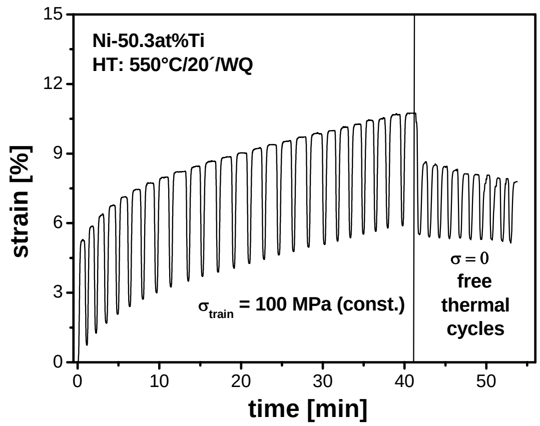


*Fig. 8: Course of strain during training and during free thermal cycles*

*Table 2: Training parameters and resulting two-way shape memory effects, $\varepsilon_{2w}$.*

| Specimen | Training parameters $N_{train}$ / $\sigma_{train}$ [MPa] | $\varepsilon_{2w}$ [%] |
|---|---|---|
| A1 | 25 / 100 | *2,0* |
| A2 | 25 / 100 | *2,9* |
| B1 | 25 / 100 | *0,5* |
| B2 | 25 / 100 | *0,9* |
| C1 | 50 / 140 | *0,7* |
| C2 | 50 / 140 | *1,5* |

The Cu-based alloy needs a higher training stress ($\sigma_{train}$) and a higher number of training cycles ($N_{train}$) than the NiTi(W) alloys. The highest two-way shape memory effect could be achieved with an annealed binary NiTi alloy, the addition of W evidently reduced strongly the TWSME size. The coarse-grained CuAlNi samples show a medium-size TWSME.

Thereby it was shown that lower strength of a sample leads to higher TWSME strain, the annealed samples showing larger effects than the cold-worked samples, the binary NiTi samples larger effects than the ternary NiTiW samples and finally, the coarser CuAlNi samples larger ones than the fine-grained samples. The reason for this is that it is harder to build up additional internal stress fields within a higher strength sample (e.g. fine grain) than in a low strength sample (coarse grain).

After training the samples were unloaded and thermally cycled several thousand times and the development of the two-way strain ($\varepsilon_{2w}$) was recorded. As can be seen in Fig. 9 the NiTi alloy has a higher two-way strain after training but there is a strong decay during the first several hundred cycles. On the other hand, the NiTiW alloy, especially in the cold-worked condition, shows a perfect stability of the size of the TWSME. The CuAlNi samples are also very stable with respect to the TWSME and could therefore be used for long-term applications.

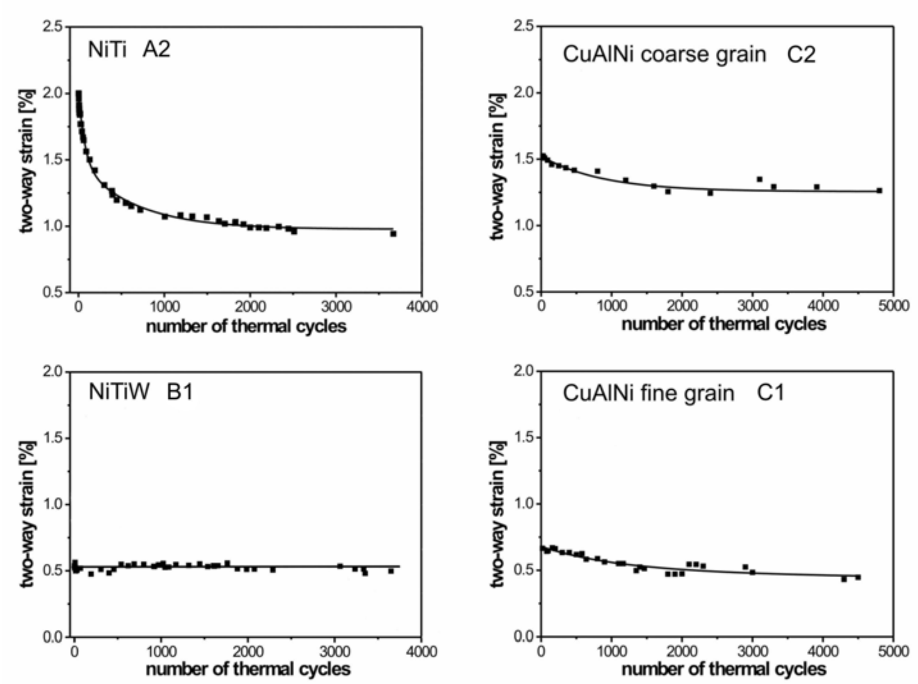


*Fig. 9: Change of two-way strain during thermal cycling*

The reason for the better stability is that the microstructures of the NiTiW and the CuAlNi samples do not change very much even after 4000 thermal cycles while the NiTi samples show a well oriented martensitic structure after the training (Fig. 10) and much less orientation after the thermal cycles (Fig. 11). The reasons are again that higher strength material does not allow easily the introduction of additional dislocations and new martensitic variants during the phase transformation from austenite to martensite as a consequence of stronger internal stress fields.

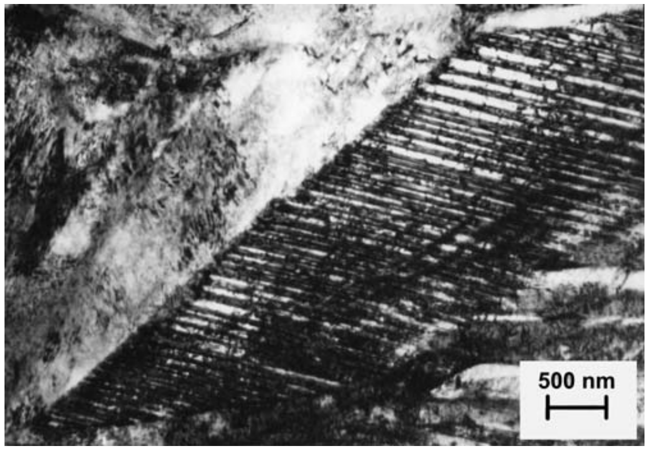


*Fig. 10: Microstructure of alloy A2 after training*

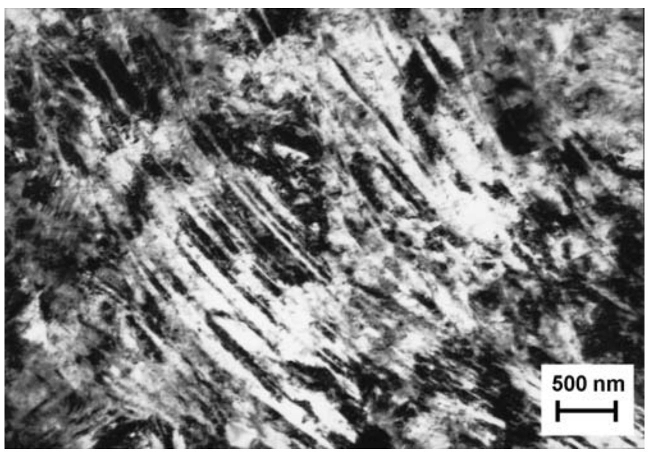


*Fig. 11: Microstructure of alloy A2 after 4000 thermal cycles*

The following results have been obtained with CuAlNi thin ribbons from the melt-spinning production: a multitude of tests was made to optimize the production parameters. The best results were obtained with the following parameters: wheel surface speed below 12 m/s, circular nozzle of 1.8 mm diameter, 5 mm distance between wheel and nozzle, 1100°C casting temperature, about $5 \cdot 10^4$ Pa Ar pressure within the chamber, about $5 \cdot 10^4$ Pa Ar overpressure within the crucible.

The ribbons range from 100 to 200 cm in average length, their width varies from 3 to 11 mm and the thickness of the ribbons ranges from 50 to 200 µm. All ribbons exhibited a one-way shape memory effect immediately after melt-spinning. An examination of the ribbons revealed that the structure was completely martensitic at room temperature. The average grain size was between 50 and 150 µm. The transformation temperatures were determined by DSC with $A_S$ = 152°C, $A_f$ = 200°C, $M_S$ = 184°C, and $M_f$ = 123°C (Fig. 12). However, these ribbons are of a low ductility which results as a consequence of a microstructure which is relatively coarse for a rapid solidification process. Tests were made on a tensile testing machine to verify this and to obtain the mechanical properties. As a result, it became evident that the samples are most likely to fracture already in the elastic region. A very fine microstructure usually results when pure Cu samples are cast on the same melt-spinning device [10,11] as used for these investigations. Hence, it was surprising that a relatively coarse microstructure was obtained in the CuAlNi alloy. The reason is evidently the lower heat conductivity of the Cu alloy compared to pure Cu. To avoid such a coarse structure a small amount of Boron was added to the alloy. As could be shown the grain size was clearly reduced to values around 10-20 μm (Fig. 13) and the ductility was substantially enhanced.

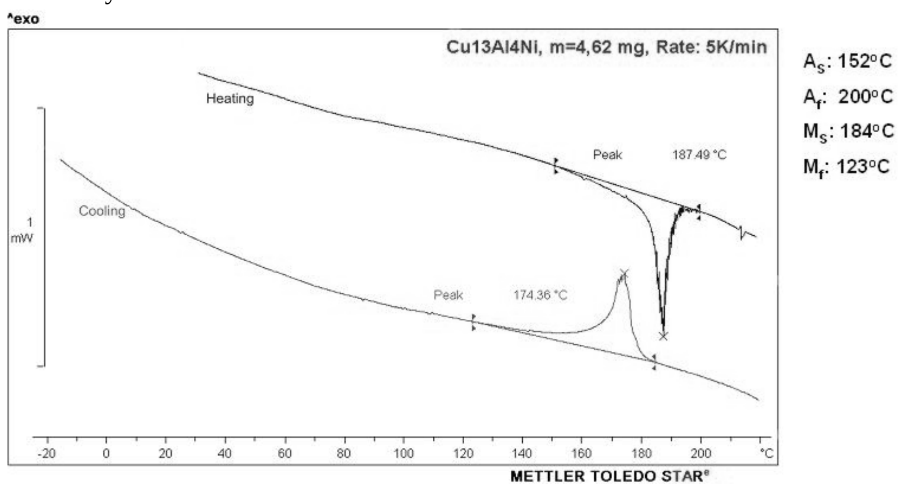


*Fig. 12: DSC analysis of a CuAlNi ribbon*

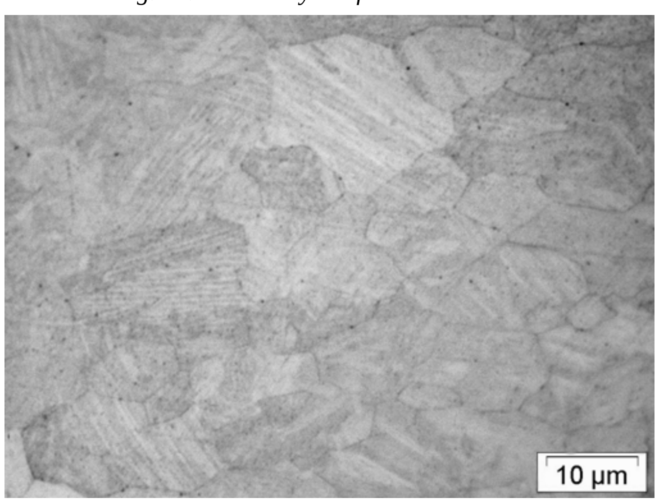


*Fig. 13: Microstructure of a CuAlNiB ribbon, etched*

**SUMMARY**

Two-way shape memory effects have been successfully introduced in three different alloy systems by training under constant stress. The TWSME immediately after training is the higher the lower the strength of a specimen. Therefore, the highest values of $\varepsilon_{2w}$ (about 3%) have been achieved in annealed NiTi samples. Most possible technical applications, however, would need long-term stability of the TWSME. In this case we get an opposite influence of the microstructural features and the strength of the material: Softer material can be trained easily to higher effect size but the stability is weak. On the other hand, samples of higher strength are harder to train, exhibit smaller TWSME values but prove to be relatively stable against functional fatigue (NiTiW and CuAlNi alloys).

In addition, thin ribbons from CuAlNi were produced successfully by melt-spinning. All ribbons exhibited a shape memory effect immediately after melt-spinning. The microstructure at room temperature is martensitic, but the grains are unexpectedly coarse, therefore only very low ductility was achieved. Adding boron to the alloy allowed to produce a finer microstructure while obtaining more ductile ribbons, which can be trained and used for application as small-dimensioned smart materials.

*Acknowledgement*

The authors want to thank Dr. Milan Bizjak and Dr. Borut Kosec (University of Ljubljana) for producing the CuAlNi ribbons by melt-spinning.

## REFERENCES

[1] S. Eucken (Ed), *Progress in Shape Memory Alloys*, DGM Informationsgesellschaft mbH, **1992**.

[2] [K. Otsuka, C.M. Wayman (Eds), *Shape Memory Materials*, Cambridge University Press, **1998**.

[3] M. Fremond, S. Miyazaki, *Shape Memory Alloys*, Springer-Verlag, Wien-New York, **1996**.

[4] T. Taburi (Ed) “Shape memory materials,” *Proceedings of the International Symposium and Exhibition on Shape Memory Materials (SMM’99)*, Kanazawa, Japan, Trans. Tech. Publications Ltd., Switzerland, **2000**.

[5] Murray, J.L. (ed.): Binary alloys phase diagrams, vol.3, AMS int., **1990**, 2875.

[6] A. Berner et al., “Microstructure of Cu-C interface in Cu-based metal matrix composite,” *Sensors and Actuators A*, 74, **1999**, 86 – 90.

[7] D. E. Ellis, K. C. Mundim, “Interstitial carbon in copper: electronic and mechanical properties,” *Philosophical Magazine B*, vol. 79, No. 10 **1999**, 1615 – 1630.

[8] I. Anzel et al., “Microstructural changes during internal carburization of Cu-Al Alloy,” *Praktische Metallographie*, 39, 8, **2002**, 401 – 413.

[9] B. Cantor, W. T. Kim, B. P. Bewlay, A. G. Gillen, *J. Mater. Sci.*, Vol. 26, **1991**, 1266 - 1276.

[10] I. Anzel et al., “Internal oxidation of rapidly solidified Cu – Zr alloys,” *Zeitschrift für Metallkunde*, 88, **1997**, 38 – 44.

[11] I. Anzel et al., “Dispersion strengthening of copper by internal oxidation of rapidly solidified Cu–Re alloys Part I: The microstructure and stability of rapidly solidified ribbons,” *Zeitschrift für Metallkunde*, 94, **2003**, 127 – 133.