## Investigation of a Cu-Zn-Al alloy with two-way shape memory effect by the cycled constrained heating/cooling technique

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The two-way shape memory effect (TWSME) is a phenomenon whereby a material can retain both high temperature and low temperature shapes, while one-way shape memory alloy can only retain the high temperature (austenite) shape. Therefore, many studies have focused on obtaining TWSME by using a variety of alloys, such as Ni-Ti [1–4], Cu-Al-Ni [5], Ni-Al-Fe [6], Ni-Cu-Ti-Hf [7], and Cu-Zn-Al [8–10].

Cu-based shape memory alloys have received more attention in the past few years owing to their low price, easy fabrication, and excellent conductivity of heat and electricity, and in our previous work [11], we have investigated the induction of TWSME by bending Cu-Zn-Al alloy samples around cylindrical structures and by employing a constrained heating/cooling technique. In the present work, in order to enhance the strength of TWSME, we have used a thermomechanical cycling method, consisting of the constrained heating/cooling technique. The alloy investigated had a composition of Cu-24.1Zn-5.6Al (wt%). The samples were prepared in an induction furnace and subsequently forged and hot-rolled. Finally, rectangular specimens with dimensions of 170 mm  $\times$  12 mm  $\times$  2.2 mm were machined from the ingot. They were heated to 800 °C, held there for 30 min, then quenched in water to room temperature. The characteristic transformation temperatures are:  $M_{\rm s} = 20$  °C,  $M_{\rm f} = 0$  °C,  $A_{\rm s} = 30$  °C, and  $A_{\rm f} =$  $61 \,^{\circ}\mathrm{C}$  ( $M_{\mathrm{s}}$  = start temperature of martensitic transformation,  $M_{\rm f}$  = finish temperature of martensitic transformation,  $A_s =$  start temperature of austenitic transformation, and  $A_{\rm f}$  = finish temperature of austenitic transformation).

The strip-shaped specimens were then bent around a cylindrical mold of 50 mm diameter placed in liquid nitrogen, and subsequently thermally heated in the temperature range of 100–240 °C, in the constrained state. The specimens were then rapidly cooled in liquid nitrogen in the constrained state, and following this, the constraint was removed. This routine was repeated up to 4 times. The strength of TWSME was evaluated by cycling the samples in the unconstrained state between temperatures below  $M_{\rm f}$  and above  $A_{\rm f}$  and a schematic diagram of the manner of measurements is shown in Fig. 1. The TWSME was evaluated using the following equation: strength of TWSME = 2(CD-AB)/EF. The microstructures were observed using a transmission electron microscope (TEM) (Jeol 200 CX), whose specimens were jet-polished with a nitric acid and methanol solution.

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In order to observe the induction of TWSME in Cu-24.1Zn-5.6Al alloy, we have varied the number of thermomechanical cycles and the constrained heating temperature respectively, in the range of 1-4 cycles and 100-240 °C. Fig. 2a indicates that the TWSME increases significantly on increasing the constrained heating temperature from 130 to 160 °C regardless of the number of cycles, revealing that the constrained heating temperature plays a significant role in improving the TWSME. It is noteworthy that the TWSME of the 240 °C-constrained heated sample is below 0.2, regardless of the number of cycles. Therefore, we find that there is an optimal range of constrained heating temperature for the induction of TWSME. Fig. 2a also indicates that the TWSME increases with the increasing number of cycles in the range of 1-4, when the constrained heating temperature ranges from 100–180 °C.

Fig. 2b shows the variation of the strength of TWSME in Cu-24.1Zn-5.6Al alloy with variation of the constrained heating time, at a constrained heating temperature of 160 °C. The strengths of TWSME with 1-cycle treatment are about 0.18 and 0.55, respectively, with constrained heating times of 60 and 120 s. The TWSME of the 120 s-treated samples is higher than that of the 60 s-treated samples, regardless of the number of cycles. We have thus revealed that the constrained heating time also affects the induction of TWSME.

We have compared the microstructures of Cu-24.1Zn-5.6Al alloys with and without thermomechanical cycling treatment, in which the sample with the treatment has a TWSME strength higher than 0.7.



*Figure 1* Schematic representation of the shape of sample. AB: cold shape after the constrained heating; CD: hot shape after the constrained heating; EF: original shape; GH: deformation imposed during the constrained heating.



*Figure 2* Variation of the strength of TWSMEs in Cu-24.1Zn-5.6Al alloys by varying the number of cycles: (a) at constrained heating temperatures of 100-240 °C and (b) at constrained heating time of 60 and 120 s.

Fig. 3a and b show, respectively, the TEM bright field image of the microstructure and the corresponding diffraction pattern of the alloy after the application of the treatment. Fig. 3a shows the new structures inclined at an angle to the existing spear or plate-like structures. Since the new structure has not been found in samples without the treatment (not shown here), we surmise that the new structure was generated by the thermomechanical cycling. From the diffraction pattern (Fig. 3b) of the "A" region in Fig. 3a, we reveal that both new and







*Figure 3* Bright-field TEM images showing the microstructures of Cu-24.1Zn-5.6Al alloys with a thermomechanical treatment. (b) The corresponding diffraction pattern ("A" region in Fig. 3a) with zone axis of  $[10 \ 3 \ 2]_{M}$  ("M1, M2" indicate the two different martensites). existing structures are the M18R martensite (in "A" region, we observe both a new and existing structure). The zone axis by calculation is  $[10 \ 3 \ 2]_M$ . The newly-induced martensite has a  $(128)_M/(128)_M$  twin relationship with the existing martensite. Additional study is necessary in order to uncover the details of the mechanism of TWSME for this particular thermomechnical treatment.

In summary, we have obtained TWSME in Cu-Zn-Al alloys with a thermomechanical cycling method: bending the alloy strips around a cylindrical mold and using a constrained heating/cooling technique. We reveal that the number of training cycles, the constrained heating temperature, and the constrained heating time, affect the strength of TWSME. TEM observation indicates that new martensite inclined to the existing martensite structures is generated in Cu-Zn-Al alloys by the thermomechanical cycling treatment. The new martensite has an M18R structure, having a twin relationship with the existing martensite.

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