DEVELOPMENT OF Cu-Al-Mn BASED SHAPE MEMORY ALLOYS-PHASE STABILITY AND MICROSTRUCTURAL CONTROL[1]

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Abstract
Phase stability and microstructural control in ductile Cu-Al-Mn shape memory alloys are presented. It was found that the addition of Mn stabilize the β (bcc) phase, which exhibits A2/B2 andB2/$L2_1$ transitions. The cold-workability can be improved by control of the degree of order in the β phase, and Cu-Al-Mn alloys with 17 at%Al show good cold-workability and shape memory (SM) properties, which strongly depend on the microstructure. In particular, an excellent superelastic strain of over 7%, which is much greater than that of other Cu-base SM alloys and comparable to Ti-Ni SM alloys, is obtained in the Cu-Al-Mn-Ni alloys by microstructural control of the recrystallization texture. The relative grain size is also an important factor for SM properties, and a good the two-way shape memory effect was obtained by simple single deformation method in a large relative grain size specimen.
Key words: Martensitic transformation; Shape memory effect; Superelasticity

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1 INTRODUCTION

Shape memory (SM) alloys are unique materials, which regain their original shape by heating (SM effect) or unloading (superelasticity). Because of these fascinating phenomena, SM alloys have been extensively investigated, and of many alloy systems, Ti-Ni alloys are widely utilized for industrial and medical products, for example, pipe couplings, sensors, guidewire and so on, due to their excellent SM and mechanical properties. Cu-based SM alloys, such as Cu-Al-Ni and Cu-Zn-Al, are commercially attractive because of their low cost and high thermal and electrical conductivity. However, they are too brittle to be sufficiently cold-worked, which is attributed to their high degree of order, high elastic anisotropy and coarse-grain structure [1,2]. Attempts have been made to improve the cold-workability by grain refining, but with limited success [1].

The present authors have found that the cold-workability can be drastically improved by control of the degree of order in the bcc β phase of Cu-Al-Mn alloys and that they exhibit SM properties due to martensitic transformation between the β_1 ($L2_1$) parent phase and β' (6M) martensite phase [3]. Moreover, microstructural control has been conducted in Cu-Al-Mn-based alloys, resulting in excellent SM properties [4-8]. In this paper, the phase stability and the microstructural control of ductile Cu-Al-Mn alloys are presented, focusing on the effect of texture and grain size on the SM properties.

2. Phase Diagram and Alloy Design of Ductile Cu-Al-Mn SM Alloy

Figure 1 shows the isothermal section at 800°C in the Cu-Al-Mn ternary alloy [9]. It is seen that the addition of Mn stabilizes the β phase. As shown in the vertical section diagram at 10 at%Mn of the Cu-Al-Mn system in Fig. 2 (a) [9], the β phase particularly extends to the low Al region. It can be found from the phase diagrams that a wide control of Al composition in the β phase is possible by the addition of Mn stabilizing the β phase.

Figure 2 (a) shows that the β phase exhibits A2/B2 and B2/$L2_1$ ordering transitions, the temperatures of which decrease with decreasing Al content,

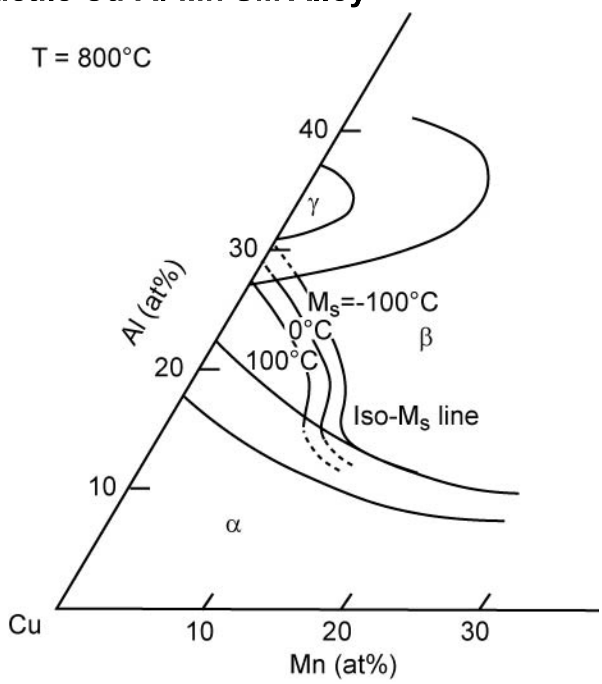

Fig. 1 Isothermal section at 800°C in Cu-Al-Mn ternary alloy with *iso-M_s* contour.

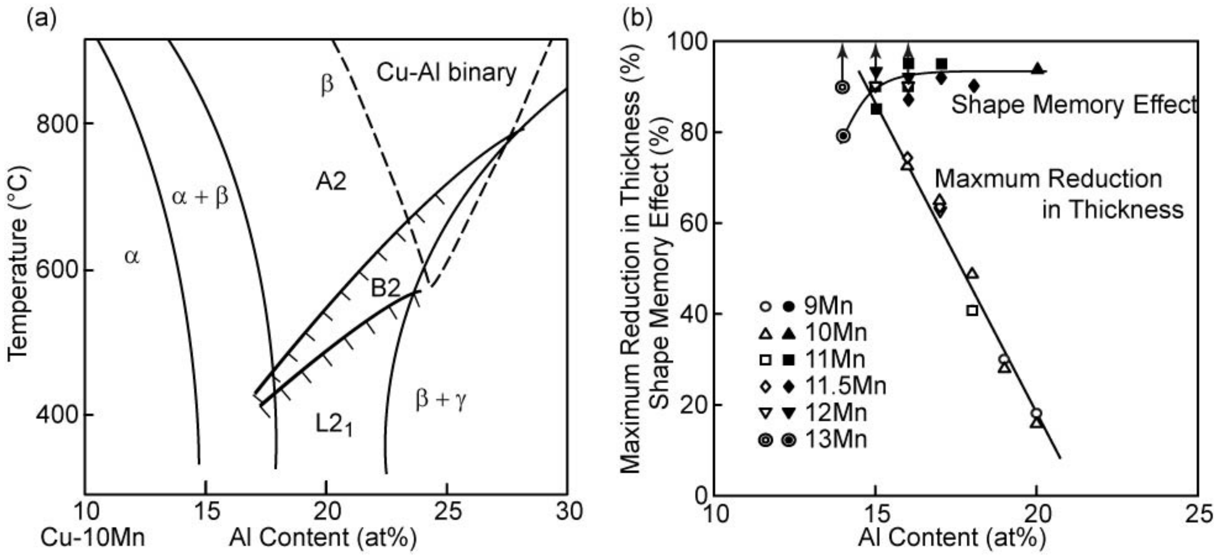

Fig. 2 (a) Vertical section diagram at 10 at%Mn of Cu-Al-Mn ternary alloy and (b) reduction in thickness before crack appears by cold-rolling and shape memory effect as a function of Al content.

and the ordering transitions are not strongly influenced by Mn content [9-11]. Therefore, the degree of order in the β phase is lowered with decreasing Al content. Figure 2 (b) shows the cold-workability evaluated by the maximum reduction in thickness before crack appears in cold-rolling and shape memory effect as a function of Al content. The cold-workability in high Al specimens is poor but improved by decreasing the Al content [3,10,11], which is clearly correlated with the decrement in the degree of order. The SM effect is also affected by the Al content and declines below 16 at%Al. It is accepted that an ordered structure is one of the essential conditions for a perfect shape recovery. The behavior of SM effect in Fig. 2 (b) is reasonable because Cu-Al-Mn alloys quenched from 800ºC is disordered A2 structure in Al content lower than 16 at% while ordered $L2_1$ structure is obtained in Al content higher than 16 at%. Considering the results of the cold-workability and SM properties, it is conclude that Cu-Al-Mn alloys with 17 at%Al are ductile SM alloys. Figure 3 shows the SM effect in $Cu_{73}Al_{17}Mn_{10}$ alloy. The pre-bent sheet fully regains its original straight shape by heating.

The iso-M_s contour based on M_s temperatures of specimens aged at 150°C is shown in Fig 1. It is seen that the iso-M_s lines curve below 20 at%Al,

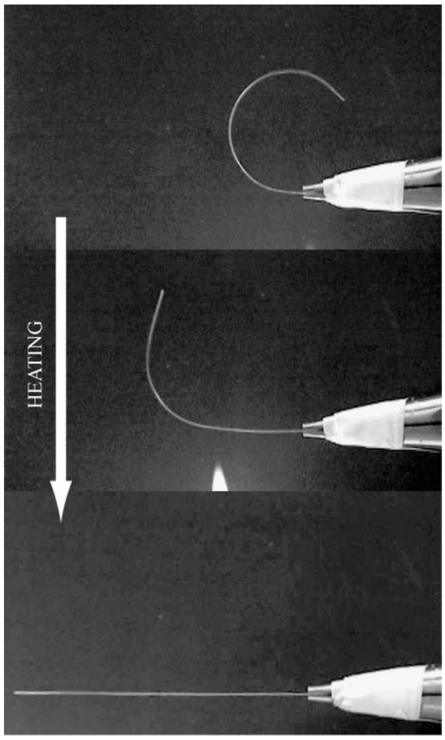

Fig. 3 Shape memory effect in Cu-Al-Mn alloy.

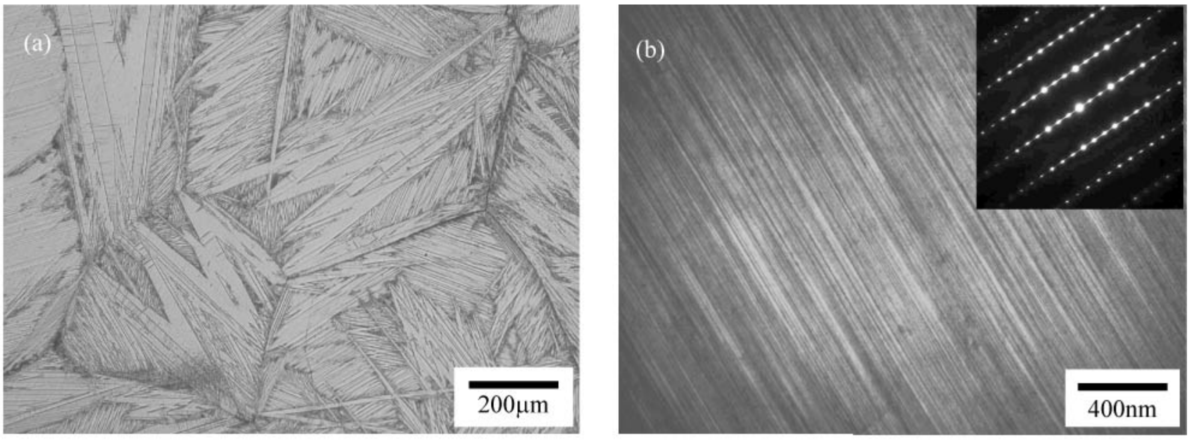

Fig. 4 (a) Optical micrograph and (b) bright field image with the corresponding selected area diffraction pattern in $Cu_{73}Al_{17}Mn_{10}$ alloy.

probably due to the decrease in the degree of order of the parent phase. This is supported by the result that the ordered reflections of $L2_1$ observed using TEM are weak and slightly diffused in the 17 at%Al alloy [3]. Figure 4 shows the microstructure of the martensite phase in the $Cu_{73}Al_{17}Mn_{10}$ alloy. Self accommodated variants are observed in the optical micrograph of Fig. 4 (a), and the crystal structure is determined to be 6M by the selected area diffraction pattern in Fig. 4 (b). The bright-field image in Fig. 4 (b) shows a high density of stacking faults due to lattice invariant deformation.

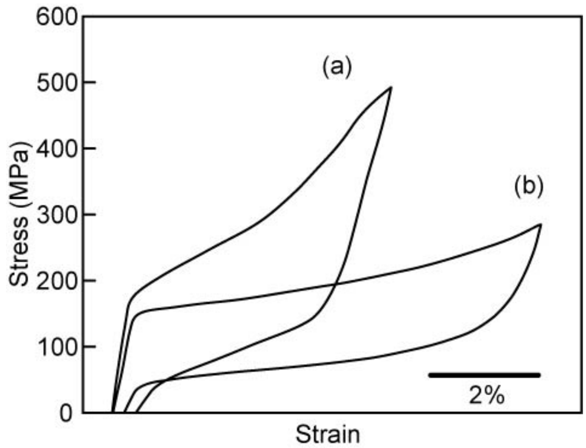

Fig. 5 Stress-strain curves in $Cu_{71.3}Al_{17}Mn_{8.7}Ni_3$ alloy with {112}<110> recrystallization texture cut along (a) transverse direction and (b) 45° from rolling direction.

3. Microstructural Control for SM Properties

The SM properties are strongly dependent on the microstructure and various microstructural controls can be conducted in the ductile Cu-Al-Mn alloys. Development of texture is one of the most important methods for improvement of SM properties because the transformation strain is orientation dependent characteristic [12-14]. It has been utilized in Ti-Ni alloys [14-17], but has not been successfully employed in conventional Cu-based SM alloys, except for in splat quenching method [14,18]. The present authors have found that recrystallization texture of {112}<110> can be obtained by thermomechanical processing, which is a combination of annealing at 600°C in the α (fcc) + β two-phase region followed by cold-rolling and subsequent solution-treatment at over 900°C in Cu-Al-Mn-Ni alloys [4]. Figure 5 shows the stress-strain curves of tensile tests in $Cu_{71.3}Al_{17}Mn_{8.7}Ni_3$ alloy with {112}<110> recrystallization texture. The specimen was cold-rolled with an 80% reduction rate and solution-treated at 900°C for 5 min followed by aging at 200°C for 15 min, and then, rectangular sheets were cut along (a) the transverse direction (TD) and (b) 45° from rolling direction (RD) corresponding to near <111> and <102> in the {112}<110> textured sheet, respectively. The stress of TD specimen is high while the superelastic strain of 45° specimen is very large with low stress. A superelastic strain of about 7%, which is about three times greater than that of other polycrystalline Cu-based SM alloys and is comparable to that of Ti-Ni alloys, is obtained. The superelastic strains of the textured Cu-Al-Mn-Ni alloy are in good agreement with the anisotropy of single crystal predicted based on the phenomenological theory [4].

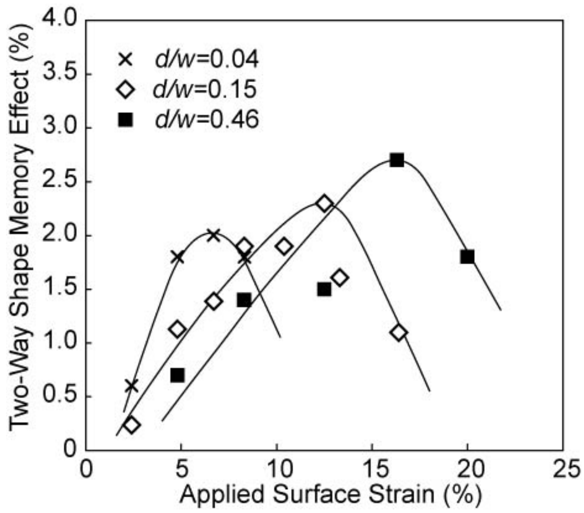

Fig. 6 Two-way shape memory effect in $Cu_{72}Al_{17}Mn_{11}$ alloy with different relative grain size, *d/w*, where *d* is the mean grain diameter and *w* is the width of the specimen.

It is known that the relative grain size normalized by specimen size influences the SM properties [19,20] and the SM strain increases with relative grain size due to the decrement in grain constraint. However, the SM strain is limited in conventional Cu-based SM alloys because intergranular fracture easily occurs in coarse grain specimens. In the ductile Cu-Al-Mn alloys, the SM properties can be drastically enhanced by increasing relative grain size and 7% SE strain was obtained in large relative grain size specimens [5,6]. Two-way shape memory effect (TWME), which is a spontaneous and reversible shape change during heating and cooling, also depends on the relative grain size. Figure 6 shows the TWME obtained by single bending deformation method [21-23] in $Cu_{72}Al_{17}Mn_{11}$ alloy with different relative grain size *d/w*, where the *d* and *w* are mean grain diameter and width of sheet, respectively. It is shown that an excellent TWME is obtained in large *d/w* specimen by applying a high revel of pre-strain. It should be noted that the excellent ductility of Cu-Al-Mn alloys enables the application of high deformation, causing the good TWME obtained by single high deformation method.

4. Concluding Remarks

The SM properties of Cu-Al-Mn-based alloys are summarized in Table 1 in

Table 1 Ms temperature, cold-workability and shape memory properties of Cu-Al-Mn based and other SM alloys.

	M_s Temp. (°C)	in Cold-Working (%)	Strain (%)	SM Effect (%)	Memory Effect (%)
Cu-Al-Mn	-200 ~ 120	>60	7.5	~10*	~2.2**(3.6)***
Ti-Ni	-40 ~ 100	~30	8	8	5
Cu-Al-Ni	-200 ~ 170	~10	2	5	2
Cu-Zn-Al	-200 ~ 120	~30	2	5	2**(0.8)***

* Surface strain obtained by a bending test
** Surface strain induced by bending deformation
*** Strain induced by tensile-deformation

comparison with those in Ti-Ni, Cu-Al-Ni and Cu-Zn-Al conventional SM alloys [2, 24-26]. Cu-Al-Mn-based alloys undergo martensitic transformation in a wide temperature range, and the cold-workability is much higher than that in other SM alloys, which is achieved by control of the degree of order in the β phase. Superelasticity and SM effect are enhanced by microstructural control such as texture, resulting in excellent SM properties. They also exhibit the TWME induced by the simplest method of single high deformation [21-23] or cold-rolling [27-29] due to their high cold-workability. It can be concluded that the Cu-Al-Mn-based alloys have high potential for practical applications.

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