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Superplasticity of Cu-Al-Mn-Ni Shape Memory Alloy*[1]

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The microstructure and superplastic behavior at 450°C and 500°C in Cu-Al-Mn-based shape memory alloys were investigated using optical microscopy and a tensile test. It was found that a fine α (fcc) + β (bcc) two-phase structure with a grain size of 3 μm in diameter can be obtained in Cu-Al-Mn-Ni alloy by annealing at 600°C. The flow stress of Cu-Al-Mn-Ni alloy depends on the strain rate and the strain rate sensitivity is over 0.3 with an elongation of over several hundred percent, which shows that the Cu-Al-Mn-Ni shape memory alloy exhibits superplasticity. For the test temperature at 500°C and a strain rate of 5×10^{-4} s^{-1}, a maximal elongation of 1150% was obtained. The formation of cavity stringers lying parallel to the tensile axis was observed and the size of the cavity was larger as the specimen was more highly deformed. [doi:10.2320/matertrans.D-MRA2007879]

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Keywords: *copper-aluminum-manganese, shape memory alloy, superelasticity, superplasticity, cavity*

1. Introduction

Cu-based shape memory alloys, including Cu-Al-Ni and Cu-Zn-Al, have been extensively investigated because of their good shape memory properties, high electrical and thermal conductivity and low cost, although Ti-Ni is the only shape memory alloy which has been widely utilized in practical applications. However, these Cu-based shape memory alloys 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)] Attempts have been made to improve the cold-workability of these Cu-based alloys by grain refining, but with limited success.[1)]

The present authors have developed ductile Cu-Al-Mn shape memory alloy based on the phase diagram. Figure 1 shows the vertical section diagram at 10 at% Mn in the Cu-Al-Mn system[2)] with the β (bcc) phase in Cu-Al binary system, where the β phase can exhibit martensitic transformation and shape memory properties. It is seen that the β phase significantly extends to the low Al content region by the addition of Mn. The A2/B2 and B2/L2$_1$ ordering transitions occur in the β phase, whose temperatures are strongly dependent on the Al content, and thus the degree of order in the β phase is lowered by decreasing the Al content. By control of the degree of order, ductile Cu-Al-Mn alloys containing Mn over 8 at% and 17 at% Al can be obtained.[3–5)] Moreover, by the combination of grain size and texture control, the Cu-Al-Mn alloys exhibit a superelastic strain of about 7%,[6–9)] which is comparable to that of Ti-Ni alloys, as well as some related functional properties such as a functionally graded property,[9)] a two-way shape memory effect,[10,11)] a damping property[12–14)] and the Invar effect.[15)]

It is known that superplasticity can be obtained at a suitable temperature and strain rate in a fine grain size specimen, and superplastic behavior has been reported in several Cu-Al and Cu-Zn alloys.[16–20)] In Cu-based shape memory alloys, superplasticity has already been reported in Cu-Al-Ni-based,[21)] Cu-Zn-Al-based[22)] and Cu-Zn-Sn-based[23,24)] alloys with fine microstructures. Recently, the present authors found that ductile Cu-Al-Mn shape memory alloys containing Ni show a very fine $\alpha + \beta$ two-phase microstructure.[6)] This fact means that the Cu-Al-Mn-Ni shape memory alloys can also be expected to exhibit superplasticity. In the present study, the microstructure and superplasticity of Cu-Al-Mn-Ni shape memory alloys were investigated.

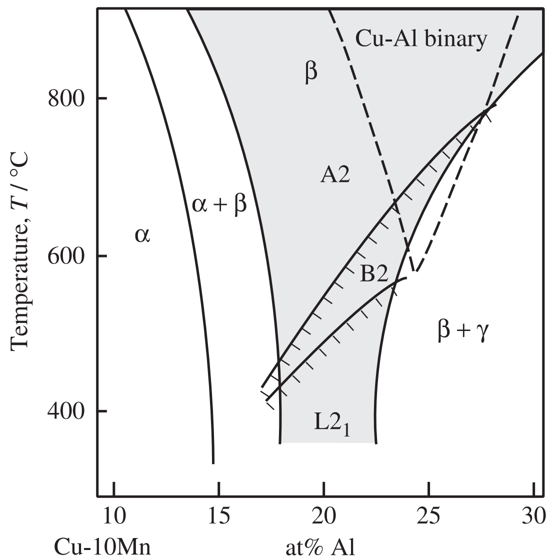

Fig. 1 Vertical section of 10 at% Mn in Cu-Al-Mn system with β phase of Cu-Al binary system indicated by broken line.

2. Experimental

$Cu_{71.5}Al_{17}Mn_{11.5}$ and $Cu_{71.3}Al_{17}Mn_{8.7}Ni_3$ alloys were prepared by induction melting under an argon atmosphere. The ingots were hot-rolled to a thickness of 10 mm at 800°C and subsequently cold-rolled to a thickness of 1.15 mm with intermediate annealing at 600°C. Specimens were cut from the sheets, and heat treatment was conducted at 600°C for 30 min or at 900°C for 15 min.

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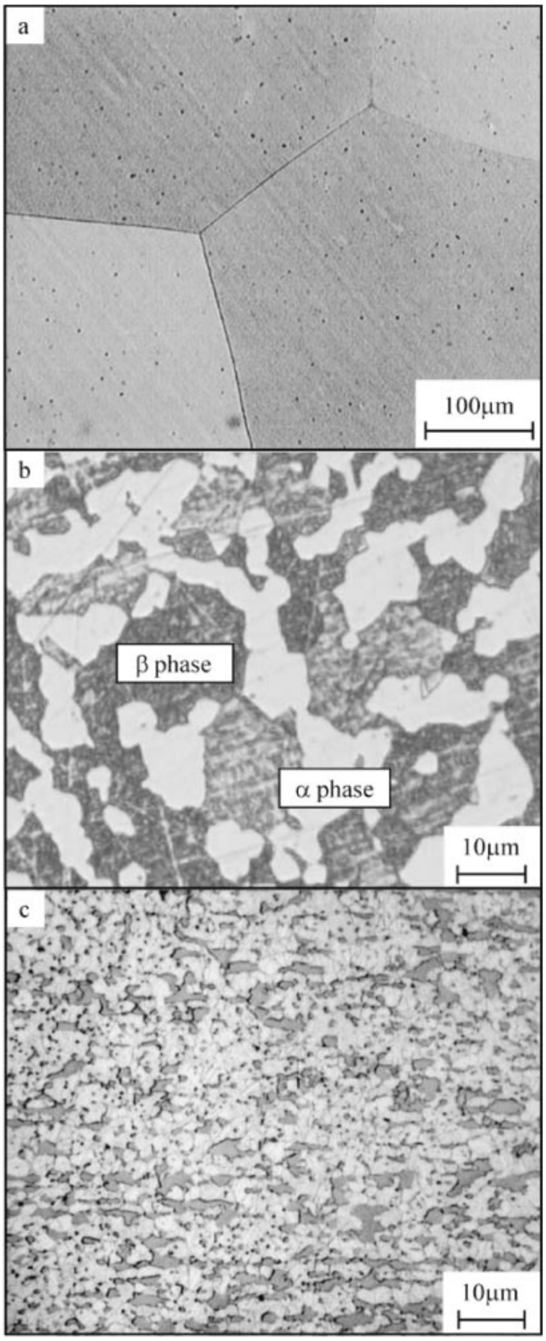

Fig. 2 Microstructure of (a) β single-phase and (b) $\alpha+\beta$ two-phase of Cu-Al-Mn and (c) $\alpha+\beta$ two-phase of Cu-Al-Mn-Ni alloy.

The microstructure was observed using an optical microscope and the volume fraction of the α phase was determined by image analysis.

Tensile tests were carried out by an Instron-type machine at 450°C and 500°C, where the tensile axis was parallel to the rolling direction of the sheet and the strain rate was constant in the range of $1 \times 10^{-1}\,s^{-1}$–$5 \times 10^{-4}\,s^{-1}$.

3. Results and Discussion

3.1 Microstructure of Cu-Al-Mn and Cu-Al-Mn-Ni alloys

From Fig. 1, it can be expected that the ductile Cu-Al-Mn shape memory alloy with 17 at% Al shows the β single phase at temperatures over about 700°C, while the $\alpha+\beta$ two-phase structure appears at lower temperatures. Since the α phase is very ductile due to the disordered fcc structure, improvement of the ductility for the Cu-Al-Mn-base shape memory alloys is possible by the introduction of the α phase in the β phase. Therefore, the annealing temperature suitable for subsequent cold-working is around 600°C and the final shape memory treatment to obtain the β single phase can be performed at temperatures over 800°C.

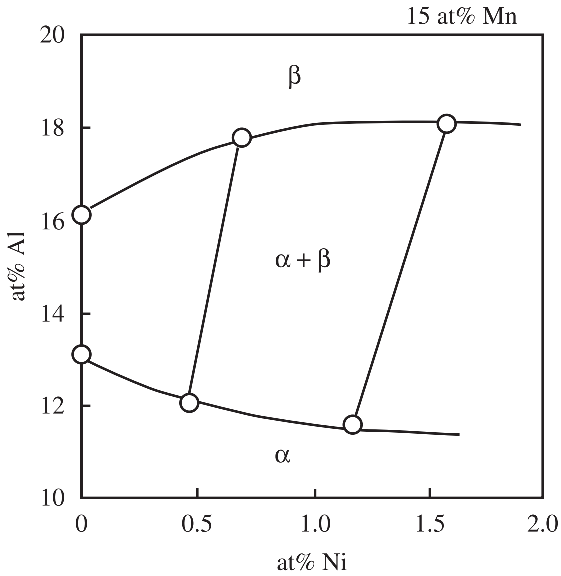

Fig. 3 Isothermal section of 15 at% Mn in Cu-Al-Mn-Ni system at 700°C.

Figures 2(a) and (b) show the β single-phase microstructure with a grain diameter of 400–500 μm annealed at 900°C for 15 min and the $\alpha+\beta$ two-phase structure annealed at 600°C for 30 min in the $Cu_{71.5}Al_{17}Mn_{11.5}$ alloy, respectively. The optical micrograph in Fig. 2(c) shows the $\alpha+\beta$ two-phase microstructure taken from the $Cu_{71.3}Al_{17}Mn_{8.7}Ni_3$ alloy annealed at 600°C for 30 min, which exhibits a much finer two-phase microstructure with a mean grain diameter of approximately 3 μm. The volume fractions of the α phase for the ternary and quaternary alloys shown in Figs. 2(b) and (c) are 42% and 64%, respectively. This result is consistent with the phase diagram shown in Fig. 3 between the α and β phases at 700°C,[25] where the partition of Mn between the α and β phases is almost equal. It is seen that the $\alpha+\beta$ two-phase region is widened by the addition of Ni and that the volume fraction of the α phase increases with the addition of Ni at Al content of 17 at%. The increase of the α phase volume improves the cold workability, and the maximum reduction in thickness before a crack appears in a sheet by cold-rolling increases from 60% to 80% by the addition of Ni.

The Cu-Al-Mn-Ni shape memory alloy with the $\alpha+\beta$ two phase microstructure, which was obtained by annealing at 600°C, seems to have a microstructure suitable for obtaining superplasticity, *i.e.*, the grain size is less than 10–15 μm.[26]

3.2 Superplasticity

The tensile test was carried out for the $Cu_{71.3}Al_{17}Mn_{8.7}Ni_3$ alloy annealed at 600°C for 30 min, whose microstructure

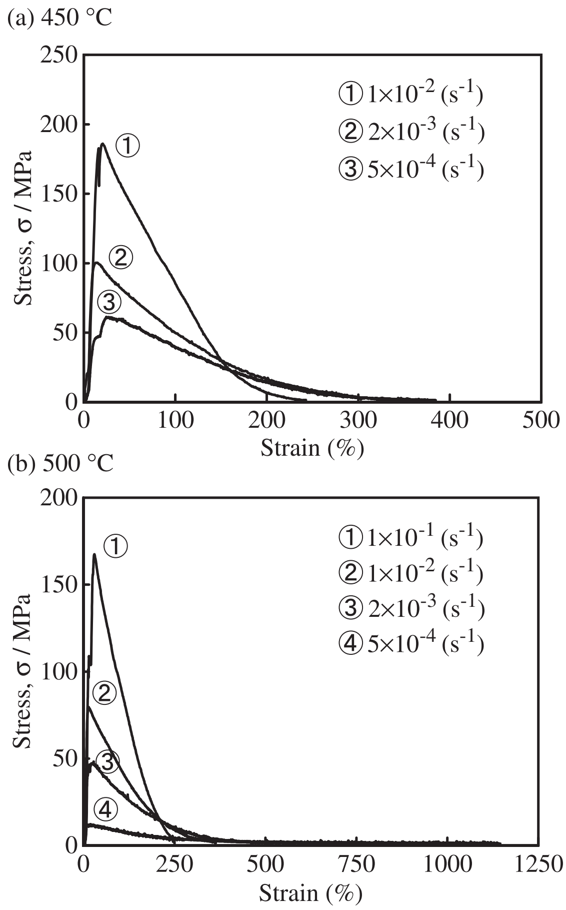

Fig. 4 Stress-strain curves of $Cu_{71.3}Al_{17}Mn_{8.7}Ni_3$ alloy at indicated strain rates at (a) 450°C and (b) 500°C.

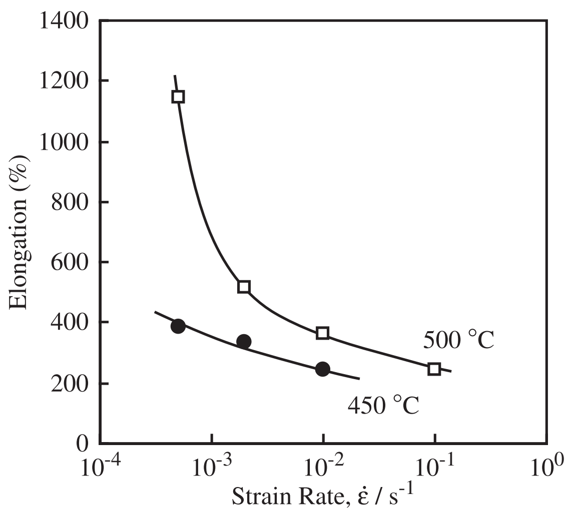

Fig. 5 Superplastic elongation as a function of strain rate in $Cu_{71.3}Al_{17}Mn_{8.7}Ni_3$ alloy.

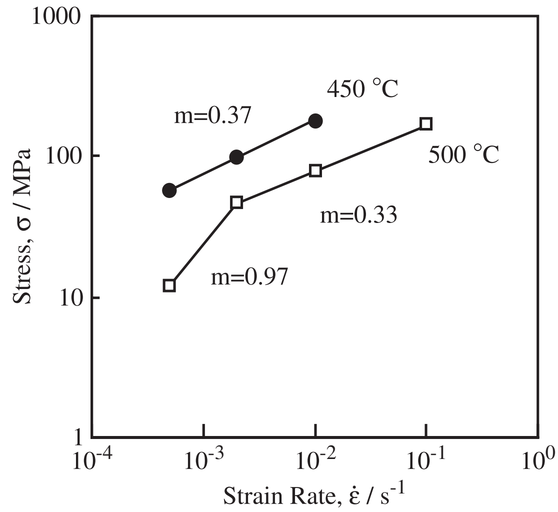

Fig. 6 Flow stress as a function of strain rate in $Cu_{71.3}Al_{17}Mn_{8.7}Ni_3$ alloy.

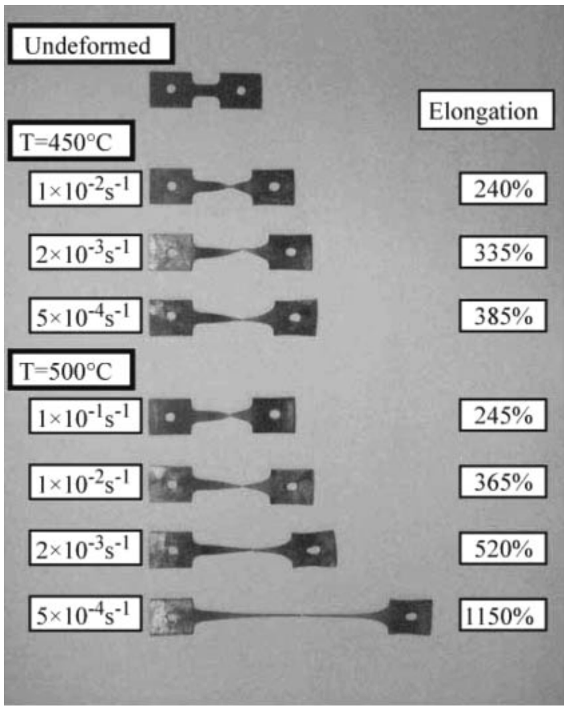

Fig. 7 $Cu_{71.3}Al_{17}Mn_{8.7}Ni_3$ alloy before and after tensile tests at various strain rates at 450°C and 500°C.

is shown in Fig. 2(c). Figures 4(a) and (b) show the stress-strain curves at 450°C and 500°C, respectively. Figure 5 shows the elongation to failure as a function of strain rate. The elongation is enhanced several hundred percent by deformation at a lower strain rate and a higher temperature; in particular, that at $5 \times 10^{-4}\,s^{-1}$ and 500°C reaches 1150%. Figure 6 shows the flow stress against strain rate. It is seen that the flow stress increases with increasing strain rate and that at the same strain rate, the flow stress at 450°C is always higher than that at 500°C. The strain rate sensitivity, *m*, at 450°C is about 0.37 and that at 500°C is over 0.33. This plastic behavior with the large tensile elongation prior to failure and the large strain rate dependence of flow stress is clearly due to superplasticity. Actually, it has been reported that the Cu-Zn superplastic alloy with a $\alpha + \beta$ two phase microstructure shows $m = 0.1$–0.2 at 400°C and $m =$ 0.2–0.4 at 500°C at strain rates of $1 \times 10^{-3}\,s^{-1}$–$1 \times 10^{-2}\,s^{-1}$.[16] It can be concluded that the Cu-Al-Mn-Ni two-phase alloy, which is similar to other superplastic Cu-base alloys, is a superplastic shape memory alloy.

Figure 7 displays the specimens before and after the

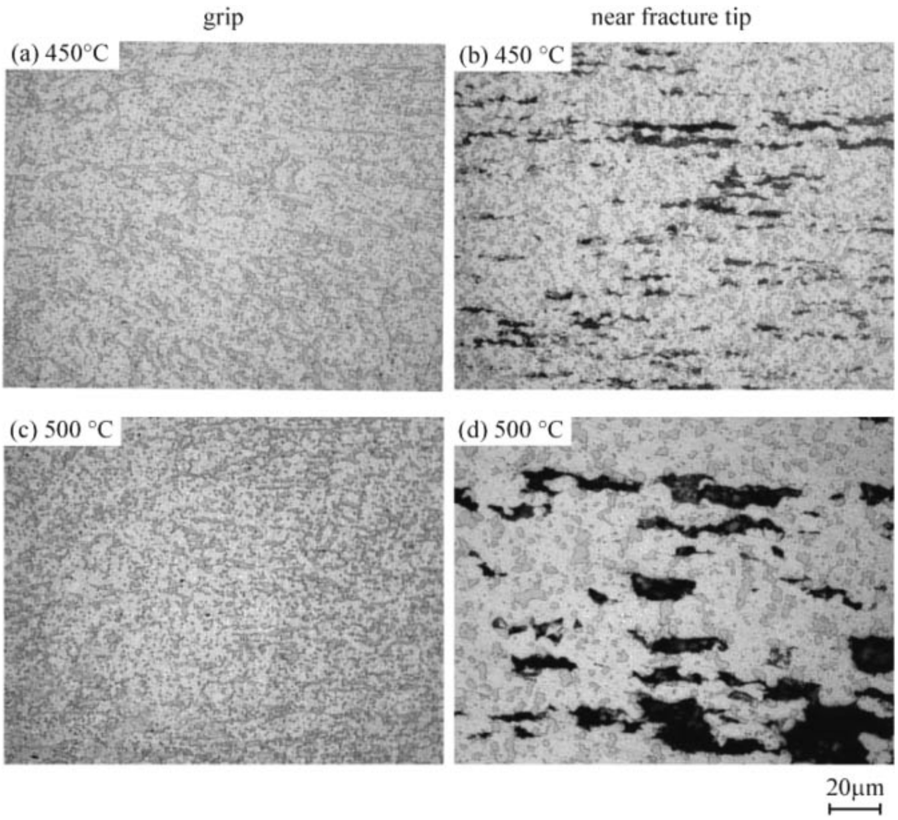

Fig. 8 Microstructures of specimens tensile-tested at indicated temperatures at a strain rate of $5 \times 10^{-4}\,s^{-1}$ with the tensile axis being horizontal.

tensile test. While necking can be observed in the specimens deformed at higher strain rates at the lower temperature, the specimens at lower strain rates at the higher temperature show a large elongation without necking.

3.3 Microstructure after tensile test

The microstructures of the specimens tested until rupture at a strain rate of $5 \times 10^{-4}\,s^{-1}$ at 450°C and 500°C are shown in Fig. 8, where the tensile axis corresponds to the transverse direction. Figures 8(a) and (c) show the microstructure near the grip of the tensile test specimens, and (b) and (d) are taken from the regions near the fracture tip. Here, the cavities are seen lying parallel to the tensile axis and the shape of grains is approximately equiaxed as shown in Figs. 8(b) and (d), which are common features in the superplastic alloys.[27] It is also observed in the specimen after the 1150% elongation (in Fig. 8(d)) that the mean size of the cavities is larger than that of the specimen subjected to static isothermal annealing (in Fig. 8(c)) and that noticeable grain coarsening occurs. This is clear evidence of strain-enhanced grain growth due to the high degree of deformation, which is consistent with conventional knowledge that the magnitude of grain growth increases with increasing strain.[26]

4. Conclusions

(1) The addition of Ni was found to be effective in reducing the grain size of the $\alpha + \beta$ two phase structure, and a fine microstructure with a grain size of about 3 μm was obtained in the Cu-Al-Mn-Ni alloy.

(2) The tensile test was carried out at strain rates of $1 \times 10^{-1}\,s^{-1}$–$5 \times 10^{-4}\,s^{-1}$ and at 450°C and 500°C, results showing that the flow stress is strain rate dependent and that the strain rate sensitivity is 0.33–0.97. The elongation to fracture is over several hundred percent and 1150% elongation was obtained at $5 \times 10^{-4}\,s^{-1}$ and 500°C.

(3) Cavities stringers lying parallel to the tensile axis were seen in the specimens tested until rupture, and larger cavities and grain growth was observed in the large strain specimen.

(4) The Cu-Al-Mn-Ni shape memory alloy exhibits superplasticity at around 500°C, which suggests that it has high potential as a high productivity of the shape memory alloy.

Acknowledgment

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