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Kinetic grain growth, shape memory and corrosion behavior of two Cu-based shape memory alloys after thermomechanical treatment

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Abstract: Metallurgical and mechanical properties along with shape memory and corrosion behavior of Cu−11.8% Al−3.7% Ni−1%Mn and Cu−11% Al−5.6% Mn shape memory alloys (SMAs) were comparatively studied. The influence of grain refinement on the properties was studied by optical microscopy (OM), scanning electron microscopy (SEM), differential scanning calorimetry (DSC), potentiodynamic polarizations and bend and tensile tests. Static recrystallization and kinetic grain growth show a rapid recrystallization in the first 15 s of annealing at 800 °C followed by grain growths. The minimum grain sizes obtained after 15 s are 90 and 260 μm for Cu−Al−Ni−Mn and Cu−Al−Mn, respectively. Tensile tests show typical three-stage curves for both alloys, and it is seen that alloys exhibit high fracture stress and strain after grain refinement. Microstructural observations show zig-zag morphology of β_1' martensite in the Cu−Al−Ni−Mn and coexistence of β_1' and γ_1' in the Cu−Al−Mn, which were confirmed by differential scanning calorimetry results. The shape memory ratios (η) of the alloys before thermomechanical treatment, and after thermomechanical annealing at 800 °C for different time up to 15 min followed by water quenching, were evaluated. In addition, corrosion behavior of alloys after grain refinement was analyzed by means of potentiodynamic polarization measurements. The results showed that the anodic reactions were dominated by dissolution of copper, and Cu−Al−Ni−Mn alloy exhibits a better corrosion resistance than Cu−Al−Mn alloy.

Key words: shape memory alloys (SMAs); grain refinement; corrosion; shape memory properties

1 Introduction

Shape memory effect (SME) and superelasticity (SE) are unique properties that proceed by thermoelastic martensitic transformation. During last decades, practical application of shape memory alloys have been progressively increased in numerous applications, such as actuators, sensors, coupling, smart systems, materials with high damping capacity, structural and medical applications [1−3]. Among the numerous shape memory alloys (SMAs), Cu-based SMAs because of their lower cost and acceptable SME and SE compared with other SMAs, raised as the most attractive alloy for practical exploitations. But many potential applications of Cu-based SMAs are restricted by brittleness nature of these alloys. The brittleness of the β-polycrystalline Cu-based alloys is due to the B_2, DO_3 and $L2_1$ ordered structure of parent β-phase and abnormally high elastic anisotropy ($A=2C_{44}/(C_{11}-C_{12})$=13 and 15 for Cu−Al−Ni and Cu−Al−Zn SMAs, respectively, where C_{ij} is the elastic stiffness) which leads to stress concentration at grain boundaries [4]. The typically large grain sizes of the β-phase in these alloys intensify this tendency to brittleness even further [4]. Many attempts have been made to improve the mechanical properties of these alloys, especially, Cu−Al−Ni SMA, through grain refinement by thermomechanical treatment [5−7] and addition of alloying elements [8,9].

Recent studies showed that Cu−Al−Mn SMAs with Al content lower than 18% (mole fraction) and Mn content higher than 8% possess good ductility which is attributed to the low degree of order in the parent phase with $L2_1$ structure [10]. Two types of order-disorder transitions, $\beta(A_2)\rightarrow\beta_2(B_2)$ and $\beta_2(B_2)\rightarrow\beta_1(L2_1)$, occur during quenching in β region. In composition range above 16% Al, $L2_1\rightarrow\beta_1'$ (6M) martensitic transformation occurs, while in composition range below 16% Al the transition from A2 to $L2_1$ is suppressed by quenching and the A2 phase martensitically transforms to the γ_1' (2M) structure [10,11]. Recently, SUTOU et al [11] investigated the effect of thermomechanical treatment

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and Ni addition on the SE of Cu−Al−Mn SMAs. The thermomechanical treatment included annealing in the FCC (α)+BCC(β) two-phase region, followed by heavy cold reduction which dominated the {1 1 2}⟨110⟩ recrystallization texture. The final grain sizes were 200 μm to 400 μm which were dependent on the Ni content, and SE strain of 7% was achieved in the textured sheets. Effect of aging [12,13] and alloying element [14,15], as well as damping properties [16−18] and martensite phases [19] in Cu−Al−Mn systems have been studied very well, but till now no reports are available on corrosion behavior of Cu−Al−Mn SMAs.

In this work, in order to obtain grain refinement of Cu−Al−Mn and Cu−Al−Ni−Mn SMAs, a thermomechanical treatment was used, and microstructure, kinetic grain growth, corrosion behavior, mechanical and shape memory properties of these alloys were comparatively studied.

2 Experimental

2.1 Alloy preparation

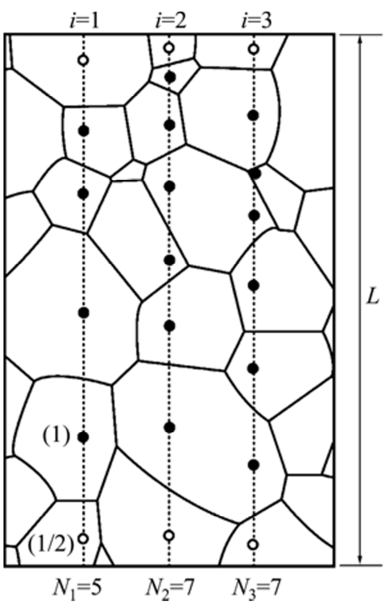
Two kinds of Cu-based SMAs, Cu−Al−Mn (AMD1) and Cu−Al−Ni−Mn (AMD2) alloys were prepared by induction melting of commercially pure Cu, Al plates and Ni, Mn powders in a graphite crucible under normal atmosphere. Glass was used as a slag to reduce the oxidation. Each ingot was remelted two times and poured in the cast iron mould with dimensions of 10 cm×5 cm×3 cm. An ice mold was placed under the cast iron mold to act as a chill and lead the shrinkage porosities to the surface of ingots. This region was then cut from the ingots. The cast ingots were homogenized at 850 °C for 12 h, and quenched in room temperature water. Chemical compositions of prepared alloys were determined by electron dispersion spectroscopy (EDS) and are listed in Table 1.

2.2 Thermomechanical treatment and characterization

Because of low cold workability of Cu−Al−Ni-based alloys, a special thermomechanical treatment was used for grain refinement of these alloys. The thermomechanical treatment was carried out. The cast ingot was hot rolled at 850 °C to a final thickness of 2 mm in 7 passes and quenched immediately after the final hot rolling pass to suppress recrystallization [5]. After 7 passes of rolling at 850 °C, the alloy temperature is still high enough and recrystallization may be occurred. So, the alloy must be quenched immediately after the final hot rolling pass to prevent recrystallization. Several specimens were prepared from the 2 mm-thick plate obtained in the first step, recrystallized at 800 °C for different time, and then quenched in room temperature water. The mean β grain size of the alloys was determined by an optical microscope (OM) and a linear intercept method [20], As shown in Fig. 1, the mean

Table 1 Chemical compositions, transformation temperatures and tensile properties of recrystallized AMD1 and AMD2 alloys

Alloy	w/%				A_s/°C	A_f/°C	M_s/°C	M_f/°C	$\sigma_{0.2}$/MPa	σ_f/MPa	ε_f/%
	Cu	Al	Ni	Mn							
AMD1	83.4	11	−	5.6	49	102	78	40	155±5	530	11
AMD2	83.5	11.8	3.7	1	80	146	122	71	170±5	620	11



$d_i=L/N_i$;

$$d=\sum_{i=1}^{3} d_i/3;$$

d_i: Average size of grains on line i;
d: Mean grain size of specimen;
L: Length of each line;
N_i: Number of grains on line i

Fig. 1 Schematic diagram for calculation of mean grain size (Grains indicated by open circles were counted as 1/2 [20])