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Effect of indium in Cu-Zn-Al shape memory alloys

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Abstract. Shape memory alloys (SMAs) are among the “smart” materials that can virtually remember their original shape; after being deformed, they may return to their initial shape through heating. The shape memory effect derives from a martensitic transformation induced by stress and/or temperature change. Copper-based SMAs are a more economical alternative compared to Ni-Ti alloys. They have low cost and various interesting mechanical and thermal properties and high practical value for the applications. In this present work, Cu-Zn-Al shape memory alloys with 0.1–0.5 wt.% In were studied. Investment casting (lost-wax casting) was performed at 1100 °C melting temperature and 650 °C mold temperature. Shape memory effect of the alloys was investigated with bending test and then heating for shape recovery. Scanning and transmission electron microscopes were used for microstructural characterization along with Energy X-ray diffraction and selected area diffraction spectroscopy. XRD measurement was also performed to understand effect of indium on microstructure. The results clearly presented that the addition of In in Cu-Zn-Al SMAs caused a precipitation of the second phase and significantly alternated the shape memory effect. The microstructure and orientation relationship of the typical and twinned martensite were discussed.

1. Introduction

Shape memory alloys (SMAs) are a group of “smart” materials that can “remember” their original shape, i.e. they can return to their pre-deformed shape after being heated. The shape-memory effect derives from a martensitic transformation due to the reversible thermo-mechanical behavior [1]. It is a diffusionless phase transformation between high-temperature austenitic phase and low-temperature martensitic phase. Copper-based SMAs are an economical alternative among SMAs because of their low cost and ease of production [2]. The Cu-based SMAs also obtain various interesting mechanical and thermal properties [3, 4] and practical value in modern applications [5-7]. Cu-Al-Ni, Cu-Zn-Al, and Cu-Al-Mn alloys are potential candidates in the Cu-based SMAs [8-10]. Their shape memory properties are largely influenced by microstructure according to the metal preparation process [11, 12]. An investment casting has been introduced to cast the Cu-based SMAs to the applicable shape which successfully retains their shape memory effects [2, 5].

In this present work, the Cu-Zn-Al shape-memory alloy with various indium additions was shaped with the investment casting process. The study was to investigate the microstructural influence using optical microscope, scanning electron microscope (SEM) along with the chemical composition analysis



by an energy-dispersive X-ray spectroscopy (EDS). In addition, XRD measurement and transmission electron microscope (TEM) were used for phase characterization. Bending test with subsequent heating was performed to follow the shape-memory effect of the alloys with the indium addition.

2. Experimental study

The Cu-Zn-Al-In shape-memory alloys were prepared from a commercial grade metals following the nominal compositions in table 1. The casting process was done by the so-called lost-wax casting technique. The alloys were melted at 1100 °C in a graphite crucible in an INDUTHERM VC400 induction furnace under nitrogen gas atmosphere. A molten alloy was then cast into a hot gypsum mold heated at 650 °C. The mold was subsequently quenched in water at room temperature. So the metal sample was suddenly cooled down. The as-cast samples were in a rectangular shape with 0.5 mm thickness.

Shape memory behavior of the alloys was investigated by bending test as schematically shown in figure 1. The sample was bent to some degrees of deformation angle (ϕ) and then heated with a lighter (roughly 700 °C) for recovering its shape. The recovery angle (θ) was measured afterward. The percentage of strain recovery, η , expressing a degree of shape memory effect (SME) was calculated following equation (1) [13]. The thermomechanical test of each alloy was repeated at least 10 times to investigate a repeatability of SME.

$$\eta = \left(\frac{\phi - \theta}{\phi} \right) \times 100\% \quad (1)$$

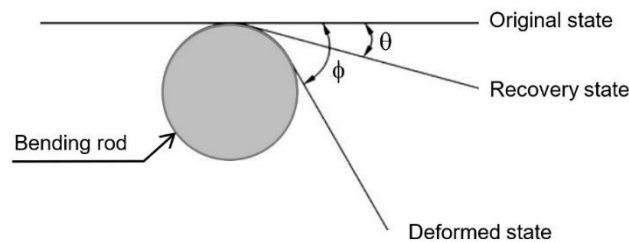


Figure 1. Scheme of bending test for shape memory effect investigation.

The samples were etched with nitric acid solution (1:1 water to nitric acid volume ratio) to reveal their microstructure prior to an observation with an optical microscope. A JEOL JSM-6335F scanning electron microscope operated at 15 kV was used to obtain microstructure images along with chemical investigation using energy dispersive X-ray spectra (EDS). X-ray diffraction (XRD) measurement was performed in a range of 20 – 60 ° with 0.02° step size using a Rigaku X-Ray diffractometer with CuK α radiation (40 KV and 30 mA). TEM specimens were prepared using FEI Quanta 3D FEG focused ion beam. Transmission electron images and selected area diffraction were examined with a Philips CM200 operated at 200 eV and equipped with 2D Phaser X-ray diffractometer.

Table 1. Nominal composition and the first stain recovery of Cu-based SMAs.

Alloy	Nominal composition (wt.%)				e/a ratio	Measured 1 st stain recovery, η (%)
	Cu	Zn	Al	In		
A	<i>bal.</i>	20.8	5.8	0.0	1.443	67 %
B	<i>bal.</i>	20.8	5.8	0.1	1.444	67 %
C	<i>bal.</i>	20.8	5.8	0.3	1.447	56 %
D	<i>bal.</i>	20.8	5.8	0.5	1.449	67 %

3. Results and discussion

The shape memory effect of the Cu-Zn-Al SMAs with indium addition was expressed in term of the strain recovery (η), in table 1, from the first bending test with subsequent heating. The investigation showed that the addition of indium maintained the recovery level of the Cu-Zn-Al SMAs at 67%. Unfortunately, with 0.3 wt.% In, SME of Alloy C was reduced to 56% strain recovery. After ten repetitions of the SME test as plotted in figure 2(a), the strain recovery decreased gradually with a number of SME tests. A proportion of the sample undergoing thermal transformation decreased due to an increase of a number of dislocations generated by the martensitic transformation and a decrease of total transformation energy [13].

The indium addition also improved the shape recovery level. In comparison with the alloy without indium (Alloy A), a reduction of η according a number of martensitic transformations was delayed when adding 0.1 wt.%In and 0.5 wt.%In in the alloys (Alloy B and Alloy D, respectively). Moreover, both Alloy B and Alloy D could survive twenty SME tests while only ten tests could be performed in Alloy A before breakage. The introduction of indium in the Cu-Al-Zn SMAs could enhance the shape memory effect and prolong their ductility. However, among the studied alloys, Alloy C (0.3 wt.%In) not only gained the lowest recovery levels at each SME test and the fastest reduction of the recovery, but could also survive only ten SME tests.

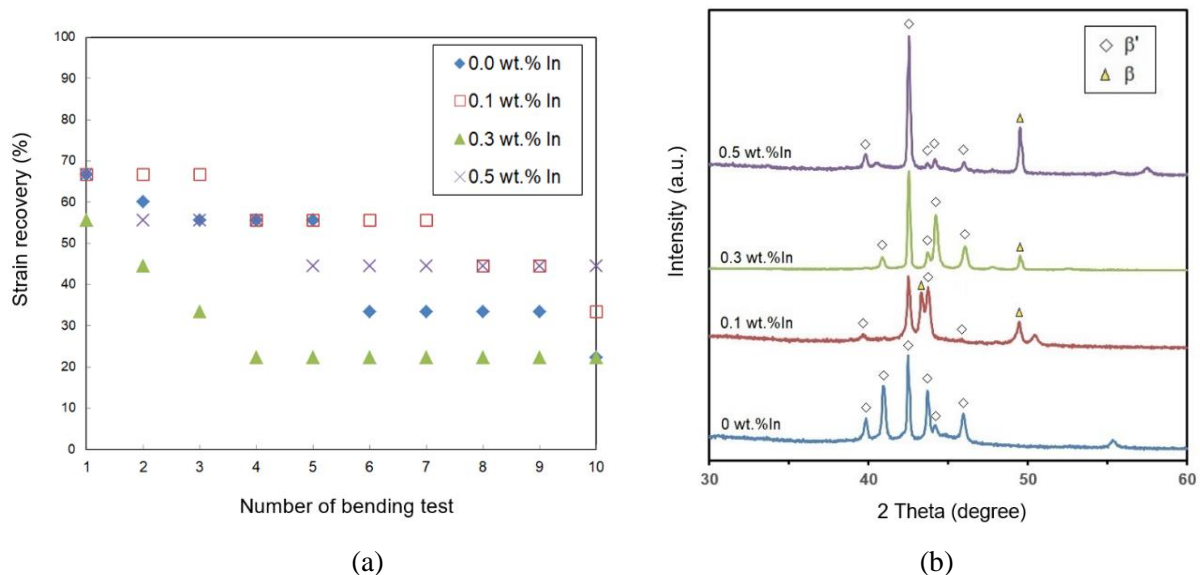


Figure 2. (a) Repeatability of SME and (b) XRD patterns of the as-cast Cu-Zn-Al-In SMAs.

The X-ray diffraction pattern of the as-cast Cu-Zn-Al SMAs with In contents in figure 2(b) indicated the β' martensitic phase present in every alloy. The β' peaks belonged to 18R type martensite which inherits from β_1 or β_3 ordered bcc structure [4, 14–16]. The as-cast Alloy A was in the β' (18R) martensite phase at room temperature. As listed in table 1, the electron to atom (e/a) ratios of every alloy was about 1.443 – 1.449, which indicated the coexistence of the α' and β' martensite morphologies [17]. They are both rhombohedral type structure with different stacking sequence [14].

With the addition of indium, the bcc β parent phase was observed in the XRD pattern which was typically found in quenched Cu-based SMAs [18]. The β peaks shifted gradually rightward with the indium contents increasing from 0.1wt.% to 0.5 wt.%. The shift indicated a more compaction of the cubic structure with the addition of indium. Moreover, the β peaks were relatively higher in comparison with that of the β' martensite peaks, with an increase of the indium contents. β phase possesses bcc structure and can be diffusionlessly transformed to rhombohedral or hexagonal type martensite [14].

Microstructures of the samples was examined using optical microscope. Figure 3 shows the optical micrographs of the as-cast Cu-Zn-Al SMAs with different indium contents. Martensite plates in V-shaped pattern in some grains and needle-like structure in others were observed in every sample. Two morphologies of the martensite structure indicated the presence of two kinds of martensite phase. 18R and 2H structures have been found in the V-shape martensite with stacking fault and in the needle-like martensite with several twin boundaries [15]. 2H martensite is inherited from β_3 parent phase [14] which could be transformed under quenching the alloys. However, XRD peaks of the H2 (hexagonal) and 18R (rhombohedral) structure superimpose so they could not be differentiated in the XRD pattern.

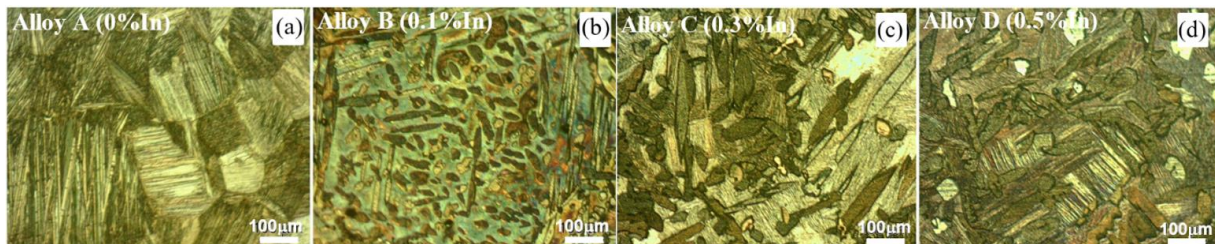


Figure 3. Optical micrographs of the as-cast alloys.

Without indium, Alloy A obtained larger grain size (more than 100 μm) which contained both forms of martensite orientated in different directions. The addition of indium induced a formation of elongated grains which corresponded with the prior β parent phase distributed among martensite matrix. Size of the parent phase increased with indium contents. The addition of indium provided more nucleation sites for the β phase, which obstructed grain growth of the prior parent phase. Grain size of the SMA alloys was then reduced significantly as shown in figure 3.

Higher magnification of SEM images were illustrated in figure 4. The matrix of all alloys showed needle-like structure of the β' martensitic phase. An amount of the prior β parent phase increased with indium content. Inside the parent phase, there was plate-like martensite with less than one micron width. The plate-like structure refers to the 2H martensite structure [15]. The presence of the β phase, as indicated by the XRD analysis, indicated that the martensitic transformation was partially occurred from quenching process during the sample preparation.

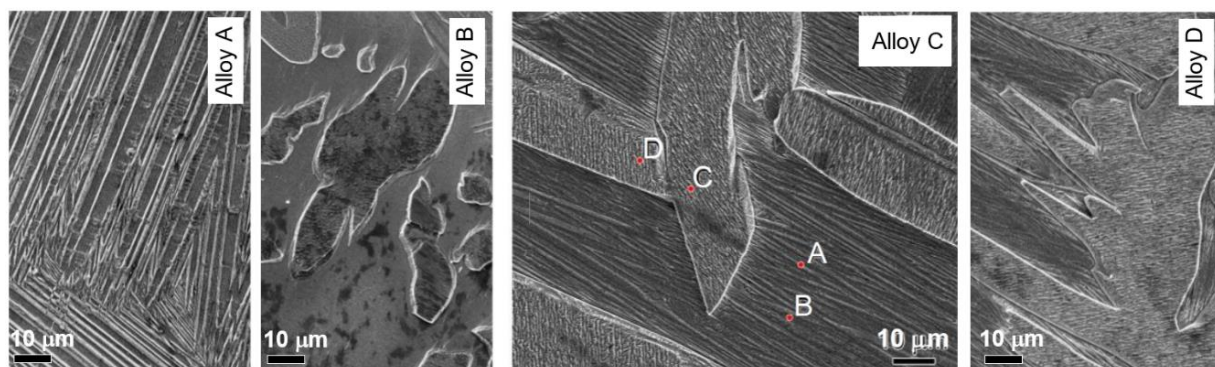


Figure 4. SEM-SE micrographs of the as-cast alloys.

To identify an elemental composition of the two-phase areas as indicated with alphabet A – D in figure 4(c), EDS analysis was performed and tabulated in table 2. The bright and dark domains in the martensite phase were marked as A and B, respectively. Likewise, the bright and dark domains of the prior β parent phase were marked as C and D, respectively. The EDS analysis revealed that Cu and Zn appeared in all domains. Copper was preferentially observed in the dark phase. Concentration of aluminum was higher in the bright area. Indium was only found in the martensitic phase and the

concentration was higher in the bright area. There was no indium observed in the parent phase both in bright and dark domains.

Table 2. EDS analysis of Alloy C at the points marked as A, B, C and D in figure 4(c).

Element	Martensite phase composition (wt.%)		Parent phase composition (wt.%)	
	Point A (Bright)	Point B (Dark)	Point C (Bright)	Point D (Dark)
Cu	70.76	79.95	77.00	78.58
Zn	17.62	14.61	17.38	16.56
Al	8.75	4.20	5.62	4.86
In	2.87	1.24	-	-

Figure 5(a) shows a bright field TEM image of the as-cast Alloy D which gained pronounced SME. Shape of the martensite phase was plate-like with a smooth and sharp phase boundary. Moreover, a ten nanometer-size substructure of martensite was observed inside a hundred nanometer-wide martensite plate. Electron diffraction patterns in figure 5(b) and figure 5(c) were obtained from the typical- and twinned-martensite at the areas marked as A and B, respectively, in figure 5(a).

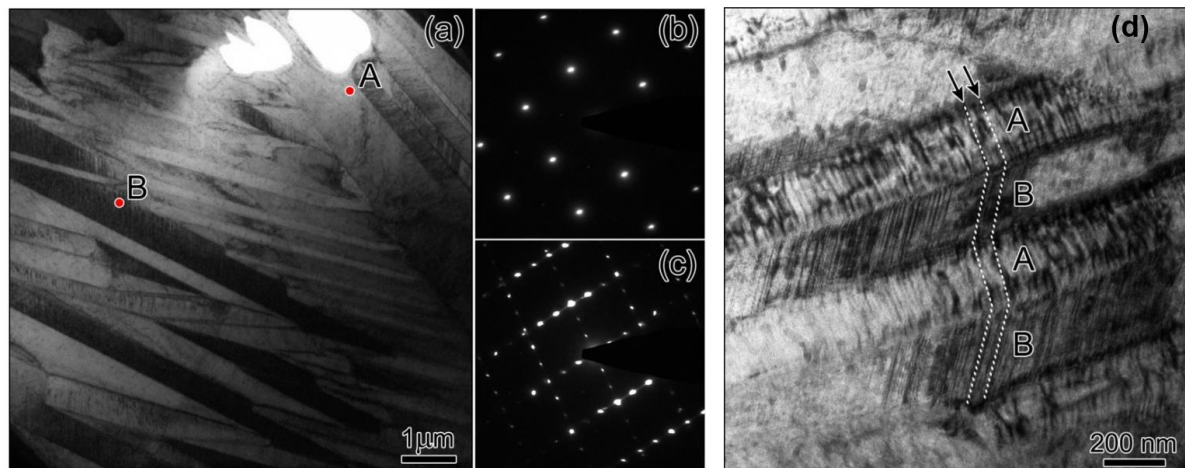


Figure 5. TEM bright-field micrograph and the selected-area diffraction patterns of the Alloy D; (a) typical martensite plate configuration, (b) and (c) SADP of martensite and twinned-martensite taken at an area marked as A and B, respectively, and (d) the twinned-martensite plate.

TEM bright-field micrograph of the twinned-martensite plate in the Alloy D was shown in figure 5(d). Dashed lines show twin planes in this alloy which confirmed the presence of 2H type martensite. The twin planes of plate A and B oriented in the directions which were perpendicular to the twin plane at 90° and 55° , respectively. The presence of extensive twinning in the alloy was one of the requirements for the excellent shape memory effect. The introduction of indium in the Cu-Al-Zn SMAs could enhance the shape memory effect and prolong their ductility because of the abundant moveable twinning.

4. Conclusion

The indium addition in Cu-Zn-Al SMAs with an investment casting process significantly influenced the shape memory effect;

- (a) The typical microstructure of Cu-Zn-Al-In alloys was plate-like martensite. The substructure of martensite consisted of twins which was important for the shape memory effect.
- (b) The investment casting process using generally for jewelry casting could retain martensite in the Cu-Zn-Al SMAs.
- (c) The amount of indium addition (0.1 – 0.5 wt.%) in the Cu-Zn-Al shape memory alloy resulted in a significant increase of shape memory recovery due to an abundant substructure twinning that accommodates the shape memory effect.

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