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EFFECT OF ALLOYING ON MICROSTRUCTURE AND SHAPE MEMORY CHARACTERISTICS OF CU-ZN-NI SHAPE MEMORY ALLOYS

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ABSTRACT

Ni-Ti and Cu–based shape memory alloys, such as Cu-Zn-Al and Cu-Al-Ni, are presently available for commercial use in shape memory applications. Ni-Ti shape memory alloys exhibit better shape memory properties and good corrosion resistance than Cu-based shape memory alloys (SMAs). However Ni-Ti in finished form is very expensive because of fabrication difficulties associated with melting and forming. In many applications, Cu-based shape memory alloys provide a more economical alternative to Ni-Ti shape memory alloys in terms of melting and designing into desired form. Cu-Zn-Ni shape memory alloys in the range of 38- 55 wt. % of Zinc and 0- 15 wt % of nickel, exhibit β- phase at high temperature, the alloys upon quenching high temperature to lower temperatures undergoes a martensite transformation manifesting shape memory effect. In the present study Cu-Zn-Ni alloys in the above said range are prepared through ingot metallurgy route on argon atmosphere. The characterization of the alloys revealed the formation martensite phase exhibited good ductility and shape memory effect. The results are given and discussed in detail.

Key words: *Cu–Zn–Ni shape Memory Alloy and Transformation Temperature and Shape Memory Effect.*

1. Introduction

Among the many alloy systems exhibiting shape memory effect (SME), Cu-Al-Ni and Cu-Zn-Al shape memory alloys (SMAs) have been studied extensively over the years [1]. Most of the copper-based shape memory alloys are easy to produce, process and are also less expensive when compared to Ni-Ti shape memory alloys. However, Cu-Al-Ni and Cu-Zn-Al shape memory alloys in the polycrystalline state are brittle and therefore, be easily worked due to the high degree of order and high elastic anisotropy of the parent β-phase (austenitic) [2].

Current Cu-based shape memory alloys [3] are derived from three binary alloy systems, Cu-Zn, Cu-Al and Cu-Sn. Among these martensitic transformation in Cu-Sn alloys are not ideally thermo elastic and suffers from a rapid degradation of a shape memory properties during ageing even at moderate temperature and it is also very brittle and composition range is less. These alloys are therefore of theoretical interest than as potential commercial shape memory alloys.

Cu-Zn based alloys containing Al, Si, Sn, Ga, or Mn as ternary alloy and Cu-Al-base ternary alloys with alloying elements such as Ni, Be, Zn and Mn [4] have been explored for their potential use. Currently Cu-Zn-Al and Cu-Al-Ni [5] shape memory alloys are commercially available and put to use in many practical applications. The alloys are suitably modified to meet specific requirements for practical use by selectively alloying with suitable quaternary and grain refining additions. Accordingly Cu-Zn-Al-Ni, Cu-Zn-Al-Ni-Mn and Cu-Zn-Ni-Ti-Mn etc [6] are developed and put use in many commercial applications. Alloys also grain refines such as B, Co, Fe, Ti, V and Zr to improve mechanical properties.

2. Experimental Procedure

2.1. Alloy preparation and composition analysis

Pure copper, Zinc and nickel were taken in right quantities from figure 1 phase diagrams to weigh 500 g of the alloy in total and were melted together in an induction furnace under an argon atmosphere. The molten alloy was poured into a cast iron mould of dimensions 150 mm x 100 mm x 3 mm and allowed to solidify. The ingots were then homogenized at 1073K in β-phase for 6hrs under an argon atmosphere. The chemical compositions of the cast alloys were

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determined using a Perkin-Elmer integrally coupled plasma-optical emission spectrophotometer.

2.2 Thermomechanical treatments and characterization

The homogenized alloy samples were hot rolled at 1073K to a thickness of 1 mm. The hot rolled samples were betatized for 30 min at 1073K and step quenched into a boiling water bath (~373K), followed by quenching them into a water bath at room temperature (~303K). Step quenching was used to avoid the quench cracks and the pinning of martensitic plates by excess dislocations retained on quenching from high temperature [7]. The microstructure and morphology of martensites formed were studied using an optical microscope.

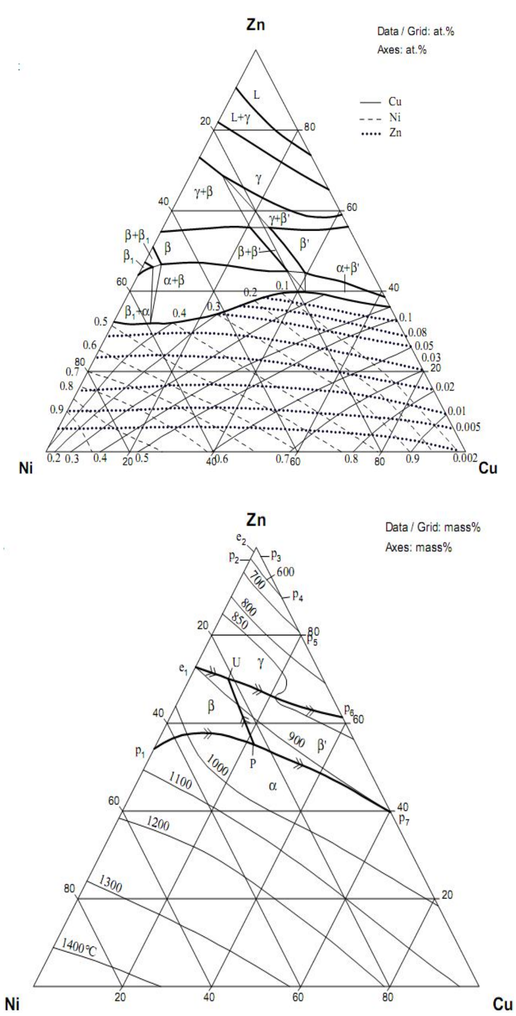


Fig. 1 (a) Isothermal section of Cu-Zn-Ni at 1048K and (b) Liquidous projections

The transformation temperatures were determined using a differential scanning calorimeter (DSC) by adopting a heating and cooling rate of 10^{o}C/min. The polycrystalline samples were analyzed by X-ray diffractometer identify the phases present in them at room temperature. The strain recovery by SME of the alloys was determined by carrying out bend tests on 1 mm thick specimens and measuring the initial and final bend angles just before heating, i.e. in the martensitic phase, and immediately after heating, i.e. in the austenitic phase of the alloys. Optical microscopes were used to study the microstructure, especially the morphology of the martensite formed. For optical microscopic studies the specimens were cold mounted using resin and were prepared by fine polishing following the standard metallographic practice polished specimens were then etched using the etchant $K_2Cr_2O_7$(2 g-$K_2Cr_2O_7$, 8 ml-H_2SO_4, 4 drops-HCl and 100 ml Water). The etched samples were thoroughly cleaned with acetone and the microstructural examination was carried out using optical microscopes.

3. Results and Discussion

3.1 Chemical composition, Transformation temperatures of Ternary Cu-Zn-Ni SMAs

The chemical compositions of all the alloys that were determined using an Inductively Coupled Plasma-Optical Emission Spectrophotometer as shown in table 1 and the corresponding Transformation temperatures on heating and cooling were determined by DSC analysis of the alloy samples. DSC for step-quenched Alloy Cu–47.22 wt.% Zn–5.71 wt.% Ni alloy. Transformation temperatures (K) above sample are Austenite start 315K and Austenite finish 333K and Martensite start 243K and Martensite finish 253K. During heating the endothermic reaction marks the transformation of martensite to austenite and during cooling an exothermic reaction marks the reverse transformation of austenite to martensite. In this alloy system it can be observed that the temperature *M*f, below which the alloy will be completely martensitic, varies from 223K to above 283K. Therefore these alloys can be suitably designed for use in different temperature and also for low temperature applications.

3.2 Shape memory effect (SME)

The shape memory effect in sheet specimens of 1 mm thickness was determined by bend test as shown in figure 2. The flat sheet specimens of the alloys were bent to a U-shape in the martensitic phase of the alloys at T< Martensite finish (M_f). The alloys were then heated to above their Austenite finish (A_f) temperature. The corresponding angles of bend before heating and after heating to above A_f temperature were measured and the percentage of strain recovery was determined. These alloy systems exhibit significant strain recovery by SME to the extent of 99% as shown in table 1.The amount of shape memory depends mainly on the amount of martensite present in the alloy and the extent of transformation of martensite to austenite. Mechanical Properties of Cu-Zn-Ni SMAs The alloys exhibit good hardness of over 189 VHN. The hardness of the alloys shown in the austenitic phase at room temperature are higher than in the martensitic phase at room temperature (~30^{o}C).

SME = θm / 180-θe Where θe = angle recovered on unloading, d = 50mm, Strain (σ) = 2%, and θ_m = angle recovered on heating

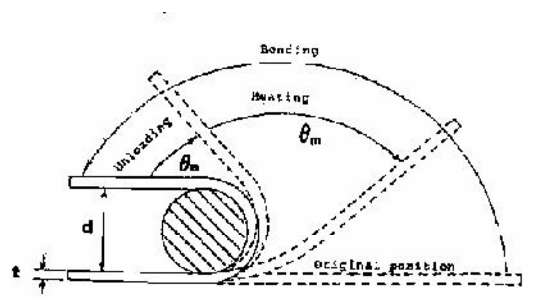


Fig. 2 Schematic diagram of the bend test to determine strain recovery by SME

Table 1. Chemical composition of Cu-Zn-Ni SMAs and shape memory effect (SME)

Alloy ID	Chemical composition (wt.%)			Strain recovery by SME in percentage
	Cu	Zn	Ni	
1	48.22	45.00	6.65	66
2	44.15	50.35	5.66	68
3	50.78	43.40	5.98	76
4	48.96	48.04	2.96	60
5	39.14	51.09	9.61	72
6	49.27	45.91	4.47	65
7	44.49	44.93	3.05	99
8	46.17	47.22	5.71	68
9	48.50	45.59	5.82	88
10	45.24	51.66	3.05	92
11	48.34	48.34	7.99	78

3.3 Phase and microstructural analysis

Figure 3a shows the optical micrograph showing parent austenitic phase of the Cu–Zn-Ni alloy samples.

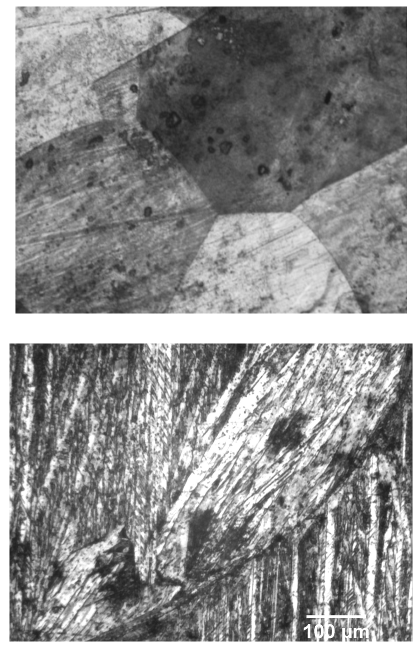
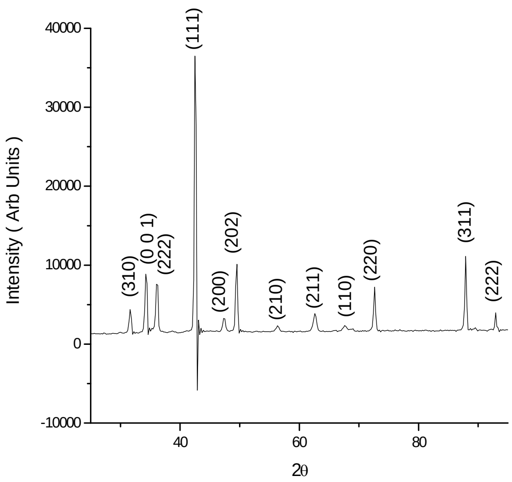


Figure.3 Microstructure of alloy Composition: (a) optical micrograph showing parent austenitic phase; (b) optical micrograph showing lath type martensite structure obtained on step quenching

The complete transformation of the parent austenitic phase to martensite can be observed in the micrographs of the alloys whose transformation temperatures lie around room temperature (~303K). Complete lath type martensitic structures with thin martensitic plates or variants are formed in these alloys as shown in figure 3b.

The different martensitic phases formed in the polycrystalline samples of the step quenched alloys were analyzed using X-ray diffractometers with Cu-Kα radiation, at room temperature. X-ray diffraction was also used to determine the phase and the contents of the specimens which homogenized at 1073K and also the sample which homogenized for 4 h. Figure 4a and 4b shows that X-ray diffraction patterns for both heat treated and compressively deformed specimens which exhibit peaks. In the case of compressively deformed specimens, peaks indicate that martensite phases generated in the specimens were also observed.



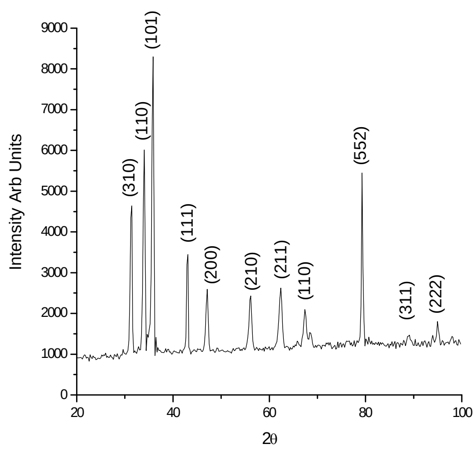


Fig. 4. X-ray diffraction patterns of Cu–Zn–Ni SMAs

4. Conclusions

i. The type and amount of martensite formed in these alloys are mainly dependent upon the amount of Zinc and Nickel in the alloys. β_1' martensitic phase is predominant in the composition range of the alloys chosen. Two kinds of martensites are observed in these alloys, i.e. β_1' (18R) martensite and γ_1' (2H) martensite with high density of twins.

ii. The transformation temperatures are highly sensitive to the variation in zinc concentrations of the alloy

iii. The alloys exhibit good strain recovery by SME. A strain recovery of up to 99% by SME was observed in these alloys.

iv. The alloys exhibit good hardness of over 189 VHN.

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