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Phase Transformation and Microstructure Behaviour of Cu-Al-Ni Shape Memory Alloys Incorporated with Cobalt Addition

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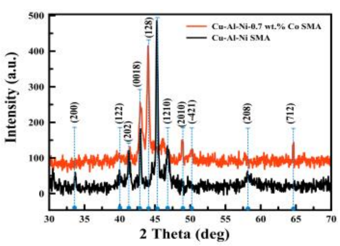
Graphical abstract



Abstract

The effect of Co addition on phase transformation temperatures and microstructures of Cu-Al-Ni SMA were investigated via differential scanning calorimetry, field emission scanning electron microscopy corresponding with energy dispersive spectroscopy and x-ray diffraction. The results revealed that the β1' and γ1' phases' morphology and orientation were varied after the addition of Co along with the presence of intermetallic compounds known as γ2. This phase was indicated using the EDS and XRD is related to the intermetallic compound of $Al_{75}Co_{22}Ni_3$. In addition, the phase transformation temperatures tend to increase with the addition of Co and this enhancement is mainly attributed to the variation of phase morphology and the existence of γ2 precipitates.

Keywords: Shape memory alloy, Cu-Al-Ni-Co, DSC, XRD

Abstrak

Kesan tambahan Co pada suhu fasa transformasi dan mikrostruktur Cu - Al - Ni SMA dikaji melalui pengimbasan kalorimeter pengkamiran ,pelepasan imbasan mikroskop elektron bersamaan dengan tenaga spektroskopi serakan dan x -ray pembelauan . Keputusan menunjukkan bahawa β1 'dan γ1'phases morfologi dan orientasi telah diubah selepas penambahan Co bersama-sama dengan kehadiran sebatian antara logam yang dipanggil sebagai γ2 . Fasa ini telah ditunjukkan menggunakan EDS dan XRD berkaitan dengan sebatian antara logam daripada Al75Co22Ni3 . Di samping itu, suhu penjelmaan fasa juga cenderung untuk meningkatkan dengan tambahan Co dan peningkatan ini adalah disebabkan oleh perubahan fasa morfologi dan kewujudan γ2 mendakan.

Kata kunci: Alloy memori berbentuk, Cu-Al-Ni-Co, DSC, XRD

1.0 INTRODUCTION

Shape memory alloys (SMAs) are functional materials that can be used as successful alternatives for conventional materials because of their superior functional properties such as shape memory effect and pseudo elasticity [1-4]. Due to these properties, it has been widely used in medical implants, micro-electro mechanical system (MEMS), actuators and damping applications [4, 5]. Among the SMAs, Cu based shape memory alloys have been significantly used because of its low cost, ease to produce and high transformation temperatures [6]. The shape memory effect and transformation behaviour of these alloys are able to be modified by varying the chemical composition, e.g., Al and Ni. For instance, reducing the aluminium contents below 12% can also improve the mechanical properties; however, increasing the Ni contents makes it behave as brittle. Thus, the composition of Cu-Al-Ni SMAs usually contains 11-14.5wt% of Al and 3-4.5 wt% Ni [7, 8]. The crystal structure of the austenite phase of Cu-Al-Ni is cubic whereas in martensite phase, Cu-Al-Ni are β'1 (18R), γ'1(2H) and α'1(6R) depending on the composition and conditions of the alloy [1, 9].

Although Cu-Al-Ni SMAs have shown good thermal stability at higher temperatures, their practical applications are still limited due to the poor workability and susceptibility to brittle intergranular cracks [10]. A number of studies have been reported about solving the issue of brittleness and enhancing the ductility of conventionally casted Cu-Al-Ni alloys, several attempts were made through grain refining that led to the martensitic transformation characteristics that can significantly be influenced either by the addition of a fourth element, such as Ti, Zr, Mn, B, Y, and V, and/or applying aging treatments [11, 12]. However, only a limited number of studies on phase transformation behaviors and microstructures of Cu-Al-Ni SMA with addition of Cobalt were conducted. Therefore, this work aims to investigate the effect of transformation temperatures and microstructure changes of Cu-Al-Ni with the addition of 0.7 wt. % Co.

2.0 EXPERIMENTAL

Cu-13wt.%Al-3.5wt.%Ni and Cu-13wt%Al-3.5wt.%Ni-0.7wt.%Co produced by melting the pure metals of Cu (99.999%), Al (99.999%), Ni(99.95%), and Co(99.95%) in silicon carbide crucible at a temperature of 1300°C. The ingot was homogenized at 900°C for 30 mins and then quenched in water in order to form martensite. The cast ingot was cut into pieces for characterisation. For phase transformation temperatures, the Perkin Elmer Pyris 6 differential scanning calorimetry (DSC) was conducted with 10 °C/min heating and cooling rates, along with an inert nitrogen atmosphere with the flow rate of 20 ml/min. The microstructures of the specimens were observed using Field Emission Scanning Electron Microscopy (FESEM) corresponding with the energy dispersive spectroscopy (EDS). The phase identifications and crystal structure determinations were carried out using a D5000 Siemens X-Ray diffractometer fitted with CuKα X-ray source with a locked couple mode; 2θ ranged between 30–70°, and 0.05° sec^{-1} is the scanning step. In order to investigate microstructures and crystal structures of the alloy, the quenched specimens were ground with different grit size using SiC papers in the following order; 200 μm, 500 μm and 1000 μm and then polished, followed by etching in a solution of 10 ml HCl, 2.5g ferric chloride acid ($FeCl_3.6H_2O$) and 48ml methanol (Ch_3OH).

3.0 RESULTS AND DISCUSSION

3.1 Microstructural characteristics

The microstructure observations of the Cu-Al-Ni, with and without Co addition are presented in Figure 1a and b. It was found that the micrograph of the base alloy contains a β`1 and γ`1 martensite phases, whereby these phases had been formed in different morphologies and orientations.

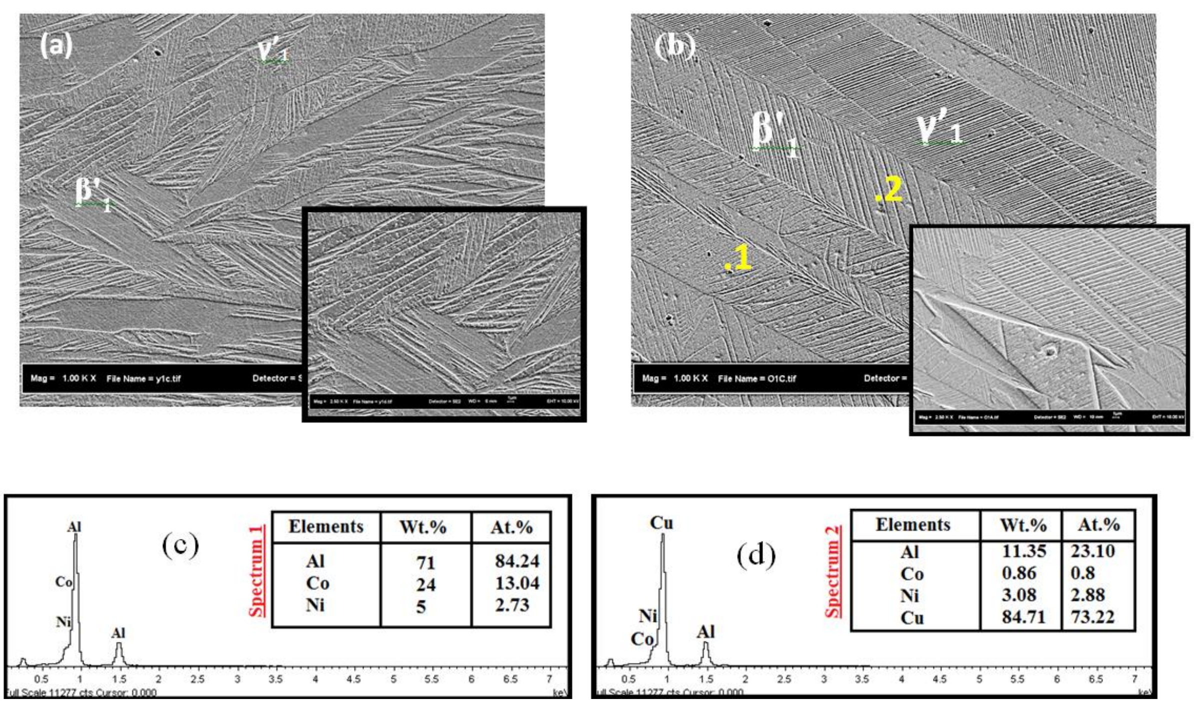


Figure 1 FESEM micrograph of alloys: (a). Cu-Al-Ni and (b). Cu-Al-Ni-Co and EDS analysis of Cu-Al-Ni-Co: (c) Spectrum 1 and (d) Spectrum 2

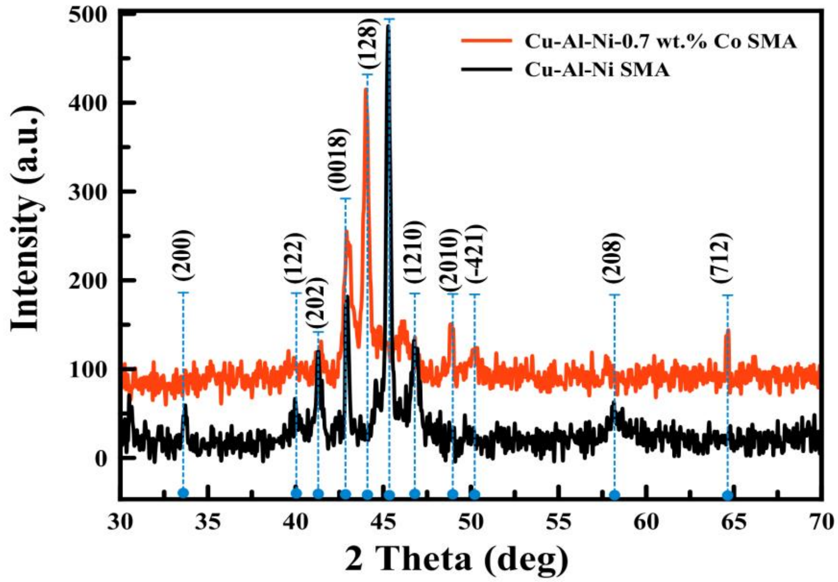


Figure 2 XRD pattern of the specimens (a) Cu-Al-Ni (b) Cu-Al-Ni-Co

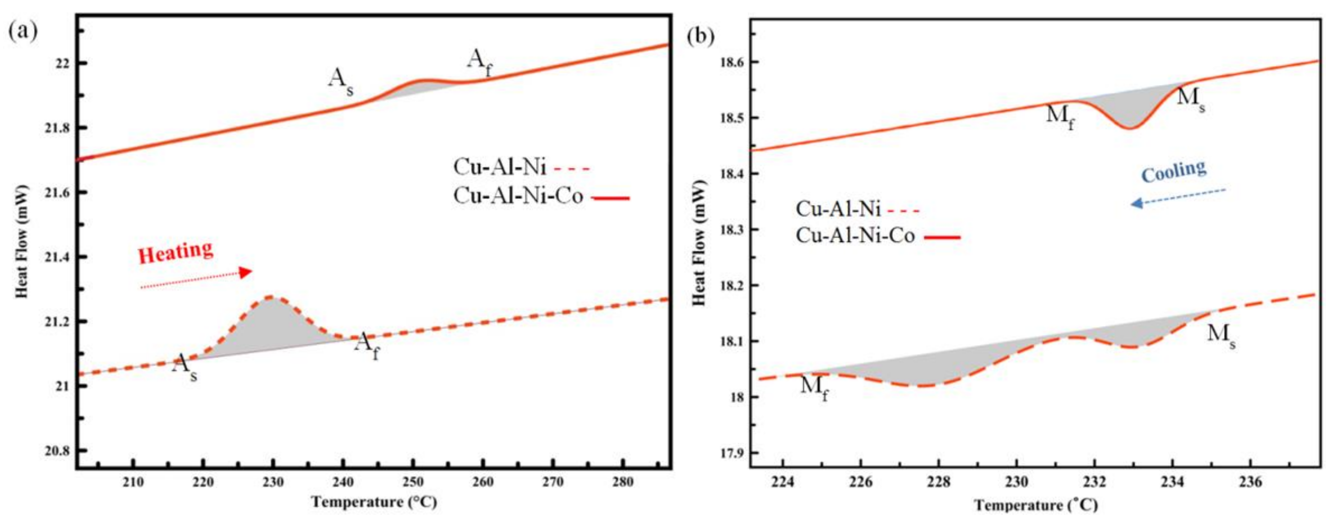


Figure 3 DSC Measurement of the Cu-Al-Ni SMA and Cu-Al-Ni-Co SMA: (a) heating curve (b) cooling curve

Table 1 Transformation temperatures of the Cu-Al-Ni SMA with and without Co addition

SMAs	Transformation Temperature (°C)				
	M_s	M_f	A_s	A_f	T_o
Cu-Al-Ni	229.86	224.12	225.8	235.49	232.68
Cu-Al-Ni-Co	234.48	231.81	240.32	244.26	239.37

The $\beta`_1$ phase was formed in small needles with self-accommodating zig-zag morphology in between the thick plates of $\gamma`_1$ martensite phase as shown in Figure 1a. With the addition of Co, the morphology of $\beta`_1$ and $\gamma`_1$ martensite varied according to the percentage of addition in which the thickness of $\gamma`_1$ plates increased with increasing volume fraction of $\beta`_1$ phase. On the other hand, there were some intermetallic compounds/precipitations that coexisted in the microstructure of the Cu-Al-Ni SMA after the addition of Co. These intermetallics are known as the γ_2 phase and in accordance to the spot scanned EDS analysis for the γ_2 -phase area, it was found that these precipitates were Co-rich, which is a combination of Co, Ni and Al in $Al_{75}Co_{22}Ni_3$ compounds [13], as shown in Figure 1. Spectrums 1 and 2 in Figures 1(c) and (d) show the EDS analysis whereby spectrum 1 is the Co-rich precipitates.

Figure 2 shows the XRD diffraction pattern of the Cu-Al-Ni SMA—with and without addition. With the Co addition, the obtained peaks are shown almost the same patterns of the base alloy, except some increasing in the value of intensity along with a slight shifting in 2θ. According to the matching process with JCPDS standards, it was found that the peaks of (200) and (202) belonged to the $\gamma`_1$, and (122), (0018), (128), (1210), (2010), (320), and (040) are represented the $\beta`_1$ phase. Meanwhile, the pattern peaks of (-421) and (712) represented γ_2 precipitates. Based on the matching of these two peaks, it was observed that these peaks belonged to $Al_{75}Co_{22}Ni_3$ intermetallic compounds.

3.2 Transformation Temperatures

The transformation temperatures and the thermodynamic parameters of the Cu-Al-Ni and Cu-Al-Ni-Co alloys were determined using DSC with heating or cooling rate of 10˚C/min. Figure 3 shows the DSC results of the alloys Cu-Al-Ni and Cu-Al-Ni-Co for forward and backward transformations and the extracted data are shown in Table 1. The phase transformation temperature measurements of DSC for the specimens were taken from 80˚C to 350˚C. Two transformation temperatures were obtained at the heating curve (endothermic reaction) in Figure 1(a), which are the austenite start temperature (A_s) and the austenite finish temperature (A_f). The other two transformation temperatures were obtained at the cooling curve (exothermic reaction) in Figure 1(b), which are martensite start temperature (M_s) and martensite finish temperature (M_f). The results revealed that the additions of Co affect the transformation temperatures. It can be seen from Figure 3 a and b that the transformation temperature shifted to higher values after the addition Co, due to the presence of γ_2 that is associated with the changes in morphology of $\gamma_1`$ and $\beta_1`$ phases. There were multi-peaks presented with the base alloy but did not exist with the modified alloy after Co addition. These peaks are related to the intermetallic transformation [12].

4.0 CONCLUSION

The effect of Co addition on the phase transformation and microstructures of Cu-Al-Ni SMA have been investigated and the following conclusions can be drawn:

1. With the Co addition, the microstructure of Cu-Al-Ni SMA varied in terms of martensite phase morphology and orientation associated with the presence of a new phase known as γ_2. According to the EDS analysis and XRD standard matching, it was observed that this phase is related to the intermetallic compounds of $Al_{75}Co_{22}Ni_3$.
2. The transformation temperatures of Cu-Al-Ni SMA were evaluated and it was found that they tend to increase after the addition of Co. This increment is attributed to the changes in the phase morphology and presence of γ_2 precipitates.

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