The Effect of Aging on the Transformation Temperatures and Microstructure of CuAlNi-Mn Shape Memory Alloys

Ali. A. Shakir¹, T. Abubakar¹*, Safaa.N.Saud²

¹Faculty of Mechanical Engineering, Universiti Teknologi Malaysia, 81310 UTM Johor Bahru, Johor, Malaysia
²Faculty of Information Science and Engineering, Management and Science University, 40100 Shah Alam, Selangor, Malaysia

Email: tuty@utm.my

Abstract. Shape memory alloys (SMAs) are one of the unique classes of smart materials, which have the ability to recover their shape when the temperature is applied. Depending on the alloy composition, shape memory alloys (SMAs) properties are largely related to the thermoelastic transformation, which occurs in the temperature range from -100 to 273 °C. This study presents the effect of aging treatment on the phase transformation temperatures, microstructure and hardness of Cu-Al-Ni-0.4 wt. % Mn SMAs. Various aging times (1-5) hour along with different aging temperatures (300 and 400 °C) were applied. The phase transformation temperatures, microstructural changes and hardness were evaluated using differential scanning calorimetry (DSC), optical microscopy and Vickers hardness test. It was found that the phase structure and properties of the alloy are varied in accordance to the aging treatment parameters. It was also observed that during the aging treatment, the grain size of Cu-Al-Ni-Mn SMA are varied in the terms of the size and thickness. Due to this, the values of hardness were observed to decrease at elevated temperatures and prolonged aging times.

1. Introduction

Shape memory alloys (SMAs) are one of the unique classes of smart materials, which have the ability to recover their shape when the temperature is applied [1]. Depending on the alloy composition, shape memory alloys (SMAs) properties are largely related to the thermoelastic transformation, which occurs in the temperature range (-100 to 273 °C) [2]. Their unusual properties are due to reversible changes of crystal lattice under influence of temperature, pressure, electrical field and magnetic, etc. [3]. The transformation of SMAs occurs between two phases’ austenite and martensite, which the phases between a high temperature called austenite and low temperature called martensite. The austenite and martensite transformation start and finish temperatures are Aₜ, Aₛ, Mₐ and Mₜ, respectively [2, 4-7]. The main types of SMAs are Ni-Ti, Cu-based and Fe-based alloys [1, 8]. The main advantages of Cu-based SMAs are their low price, easy fabrication, excellent electrical and thermal conductivity and high transformation temperature compared to other SMAs [8]. The properties of CuAlNi alloys are superior to those of CuZnAl alloys due to their wide range of useful transformation temperature and small hysteresis [9, 10]. Therefore, CuAlNi alloys more suitable to work in high temperature applications. CuAlNi shape memory alloys are less prone to the stability of the obtaining phase due to the high brittleness that may relate to the type and structure of this phase that may obtain a limit by the
applications of these alloys [11, 12]. To overcome this problem, there are two ways; the addition of grain-refiners to the melt is one of the most common methods used to refine the grain size of the alloys that are produced in bulk [13-15], and apply aging treatment [16,17], which they are able to adjust the phase diagram and improve the mechanical properties. The present paper is focused on the microstructure and transformation temperature variation of CuAlNi-Mn SMAs alloys after different aging conditions were applied, such as aging time and temperatures.

2. Experimental procedure

The alloy used for this study was prepared by melting the metals of Cu, Al, Ni, and Mn in induction furnace and then pouring into a mild steel mold with a rectangular ingot shape of 270mm x 50mm x 20mm. The chemical composition analysed using an inductively coupled plasma mass spectrometry (ICP-MS) as Cu-11.9 wt. % Al-4wt. % Ni-0.4wt. % Mn SMA. After preparing the samples from the ingot by EDM wire cutting with a final dimension (10mm×10mm×5mm), the samples were homogenized at 900°C for 30 min and then quenching in water bath. Followed by, the aging treatment process performed for two groups of CuAlNi-Mn: these groups consist of five samples treated at different aging temperatures of (300 and 400)°C for various aging time of (1-5) hr and the aged samples were quenched in water. The microstructure in terms of grain size and morphology was observed by using an optical microscope. The Vickers method with a load of 10 kg and 20s was used to measure the hardness of samples.

3. Results and discussion

3.1 Transformation temperature

In order to determine the phase transformation temperatures of the CuAlNi-Mn shape memory alloy, DSC analysis was carried out. All the transformation temperatures were according to Figure 1. It is well known that SMAs undergo a thermally induced austenite ↔ martensite transformation characterized by the critical temperatures; A_s, A_f, M_s, and M_f. Here A_s and A_f refer to austenite transformation start and finish temperatures, respectively, during heating while M_s and M_f refer to martensite transformation start and finish temperatures, respectively, during cooling.

![DSC result of unaged and aged samples at 300°C.](image)

Small peaks were identified in the DSC curves as shown in Figure 1. An endothermic peak was observed in the temperature range of 238-245°C, and an exothermic peak was observed in the temperature range
of 230-245°C for unaged and aged samples. These peaks are most likely corresponding to the reverse martensitic transformation and forward martensitic transformation. From the obtained result of DSC, the transformation temperatures and the value of the heat flow effected directly on the austenite ↔ martensite transformation curve in the shape and location. The transformation hysteresis ($A_f$-$A_s$) and ($M_s$-$M_f$), with aging temperatures, remained almost constant. From Figure 2 for aging temperature at 300°C and 400°C noted slight variations in transformation temperatures at increasing aging times at aging temperatures.

![Figure 2](image)

**Figure 2.** Changes of transformation temperatures with various aging times in CuAlNi-Mn alloy a) at 300°C and b) at 400 °C.

### 3.2 Grain size and hardness

#### 3.2.1 Grain size.** Figures 3 and 4 show the optical micrograph results for unaged and aged treatment at different temperatures; 300 °C and 400 °C and at different times (1, 2, 3, 4 and 5 hrs). The aging parameters were chosen based on the previous research [18]. All samples were etched using solution consist of 2.5g (FeCl$_3$.6H$_2$O) and 48ml methanol in 10 ml HCl for 20 seconds. Depending on the results shown from previous figures of optical micrographs for CuAlNi-Mn shape memory alloys (SMAs), we can calculate the average value of longitudinal grain size before and after aging [19], for aging we have two aging; temperatures 300 and 400 °C, and five aging times (1hr, 2hrs, 3hrs, 4hrs and 5hrs). It can be observed that grain size increased with increasing the aged temperature. The grain before aged was (173µm), and at the applying heat-treatment at temperatures 300 and 400 °C, the grain size became at first hour (217.9 and 258.33 µm) and then started to increase with increasing duration of temperatures 300 and 400 °C five hours for each temperatures (302.5 and 290 µm), respectively. From Figure 3, overall it is shown that upon the aging treatment, the grain size increased with increase the aged temperature, the time of aging treatment influence on the grain boundary. The grain size in the optical micrographs increased with increasing the time of aging of each aging temperature compared with unaged sample. The similar optical micrograph changes observed for the aging temperature at 400 °C.

#### 3.2.2. Hardness.** The value of Vickers hardness for aged CuAlNi-Mn shape memory alloys for 300°C and 400°C at five different aging times were investigated. The effect of aging time and aging temperature on the hardness of the CuAlNi-Mn shape memory alloys are shown in Figure 4. As overall the aging effect exhibits the decreasing in Vickers hardness value with the increasing of aging time at 300°C and 400°C. The value of hardness is highest for unaged specimen which is 360 MPa, while when undergo the heat-treatment the value of hardness starts to decrease. It proved that the value of hardness not only
depend on temperature but also depend on the time of aging treatment. Overall the value of hardness is actually related to the changes of microstructural during aging where the microstructure possesses decreasing in grain size lead to increase the value of hardness as Figure 5.

**Figure 3.** Optical micrographs of unaged and aged samples of CuAlNi-Mn (SMAs) at 300 ºC and different aging times
Figure 4. Optical micrographs of unaged and aged samples of CuAlNi-Mn (SMAs) at 400 °C and different aging times
4. Conclusions

As conclusions, the aging time and aging temperature influence the transformation temperatures, grain size and hardness of the CuAlNi-Mn shape memory alloy. The transformation temperatures (A_s, A_f, M_s and M_f) had a slight variation with increasing aging time of each aging temperature whereas the grain size was observed increasing with the increase of the aging temperatures and aging times. The values of Vickers hardness were observed to decrease at elevated temperatures and longer aging times.

Acknowledgement

The authors gratefully acknowledge the financial support for this research provided by Ministry of Higher Education (MOHE) and Universiti Teknologi Malaysia under Fundamental Research Grant Scheme (FRGS) vote number 4F945.

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Figure 5. The effect of aging time and aging temperature; (a) on the hardness and (b) on grain size