Thermal stability and some thermodynamics analysis of heat treated quaternary CuAlNiTa shape memory alloy

Mediha Kök¹, Ibrahim Nazem Qader¹,², Safar Saeed Mohammed¹,², Ecem Öner¹, Fethi Dağdelen¹ and Yildirim Aydogdu³

¹ Firat University, Faculty of Science, Department of Physics, Elazığ, Turkey
² University of Raparin, College of Science, Department of Physics, Rania, Sulaimanyah, Iraq
³ Department of Physics, Science Faculty, Gazi University, Ankara, Turkey

E-mail: ibrahimnazm@raparinuni.org

Keywords: heat treatment, thermal cycling, HTSMAs, CuAlNiTa, quaternary shape memory alloy

Abstract
This study presents the heat treatment effect on a quaternary Cu₇₉Al₁₃Ni₄Ta₄ (wt%) shape memory alloy. The induction technique was used for melting the alloy and then four pieces of the alloy were heat-treated at (673 K, 873 K, 1073 K, and 1273 K) for one hour. Some physical parameters were characterized using DSC, XRD, and SEM-EDX. The as-cast and heat-treated samples were studied in terms of phase transformation temperatures, enthalpy change, entropy change, Gibbs free energy, and elastic energy. The transformation temperature was increased by applying heat treatment. Martensitic phase transformation at heat treatment temperature of 1273 K was not observed. Besides, after rising heat treatment temperature, some new phases such as $\gamma'$ and $\beta'_1$ were specified in XRD patterns and SEM images. Generally, for heat-treated samples, the transformation temperature remains almost constant after the 3rd cycle. However, the thermal stability of the as-cast alloy was not affected through thermal cycling.

1. Introduction

Recently shape memory alloys are widely used in modern technological applications such as automotive, aerospace, robotics, and biomedical applications [1, 2], because of their well-known properties (superelasticity and shape memory effect), which gives them the ability to return to their original form after deformation [3, 4]. In all applications, the effect of temperature on material characteristics is one of the most important factors, especially for the production of primary materials. Although Low-Temperature Shape Memory Alloys (LTSMAs) have transformation temperatures below 100 °C, High-Temperature Shape Memory Alloys (HTSMAs) can operate at the temperature range of 100 °C [5, 6].

After NiTi family, Cu-based SMAs are the most alloy that has attracted the most attention in the technology and industry, because it can be handled easily, and its operation does not need more cost price compared with the other types of SMAs [7]. CuAlNi is the best type of Cu-based HTSMAs because it has high transformation temperature and thermal stability. CuAlNi SMAs can be used for temperatures around 200 °C, while NiTi and CuZnAl-based alloys can be controlled for temperatures about 100 °C [8, 9]. On the other hand, Cu-based SMAs have poor thermal stability, thermal conductivity, and some mechanical properties compared to the other types of SMAs, however, these properties can be improved by adding third and fourth chemical elements [7, 10–12]. Saud et al observed that the porosity density and grain size was decreased by adding 2 wt% of Ta to Cu–Al–Ni, while its transformation temperature and the corrosion resistance was increased [11]. Dagdelen and colleagues reported that the grain size and precipitations were decreased through doping CuAlCr alloy with Ni element [13]. In addition, it is reported that microhardness and precipitate particles are increased by substituting Cu with Cr element in CuAl-based SMA [14].
In this study, 4 wt% of tantalum was added to ternary Cu_{83−x}Al_{13}Ni_{4} SMA, and the effect of heat treatment has been investigated on transformation temperature, microstructure, and some other thermodynamical properties. The stability of the alloy was studied by applying 10 complete thermal cycles.

2. Experimental procedure

CuAlNiTa SMA was produced accurately using high pure powder of primary metal elements, which includes 79% wt Cu, 13% wt Al, 4% wt Ni, and 4% wt Ta. The powders were pelletized after mixing the powders and pressed with a mechanical hydraulic compressor (SPACAC). The pellets specimens were melted using the induction melting furnace. The production process was completed after quenching the sample into ice-water. To study the effect of heat treatment on CuAlNiTa SMA, the ingot was cut into some small pieces and kept them at 673 K (sample A), 873 K (sample B), 1073 K (sample C) and 1273 K (sample D), for one hour. Then, the effect of heat treatment on phase transformation temperatures (PTTs) and some thermodynamics parameters, such as entropy change, enthalpy change, Gibbs free energy, and elastic energy was investigated using Perkin Elmer Sapphire Differential Scanning Calorimetry (DSC) under the argon atmosphere at 10 °C min⁻¹ heating–cooling rate. In room temperature, the XRD was performed to analyze the crystal structure and different phases of CuAlNiTa SMA for as-cast and heat-treated samples. In addition, the microstructure of treated alloys was investigated using scanning electron microscope (SEM) and energy dispersive scanning x-ray (EDX), model (EVO 40XVP), also to obtain a clear microimage the specimens were firstly polished mechanically and then they etched with 20 ml HCl–96 ml methanol–5 gr Fe₃Cl–H₂O solution.

3. Results and discussions

3.1. Phase transformation temperature and thermodynamic properties

The DSC measurements were performed for thermal analysis of all the samples. Figure 1(a) shows the typical DSC curve of as-cast CuAlNiTa alloy. Since the austenite and martensite transformation temperatures are above 400 K, so the alloy can be classified as high-temperature shape memory alloys (HTSMA). Table 1 summarizes the PTTs including austenite start (A_s), austenite peak (A_p), austenite finish (A_f), martensite start (M_s), martensite peak (M_p), martensite finish (M_f) temperatures, and the enthalpy change of phase transformation in both heating/cooling processes. The obtained results showed that all parameters affected by the heat treatment process. To show the thermal cycling behavior, the as-cast sample was subjected to 10 cycles for both exothermic and endothermic processes with a 10 K min⁻¹ heating/cooling rate (figure 1(b)). The width of the peaks stays constant, while both austenite and martensite peaks start to shift to the higher temperature by increasing the number of cycles. Also, the vibrations in the heating peak were disappeared after completing the first cycle. In addition, sample D has lost its shape memory characteristics, thus, DSC showed peak through neither heating nor cooling process (figure 1(c)). There can be several reasons why martensitic transformation does not occur at 1273 K heat treatment temperature. First of all, this temperature (1273 K) is close to the melting zone and there is a phase transition in this zone, e.g. it can be seen this phase transition in figure 1(c). This phase transition causes the CuAlNiTa alloy to lose its shape memory property. In addition, the precipitation phase in the martensite phase effect the transformation, and thus the composition around the phase is altered. Also, there are interfaces phases in the martensite variants [15, 16].

Figure 2(a) illustrates that the PTTs have been generally increased by applying heat treatment on the alloys (except for sample D). The alloy that aged at 673 K, has the largest temperature hysteresis, however, its value was decreased by increasing the heat treatment temperature (figure 2(b)). In this study, the chosen heat treatment temperatures are before the eutectoid phase decomposition, which is taking place at 673 K. The eutectoid phase degradation occurs at 838 K [17], thus, it can be concluded that a significant decrease in the value of hysteresis has occurred after the eutectoid transformation took place. In addition, while the value of A_p (figure 3(a)) and M_p (figure 3(b)) increase gradually with increasing the thermal cycling, in all heat-treated samples these values have diminished. It is well observed that after applying 3 to 4 thermal cycling all cases have been stabilized. Also, the value of M_p is converged by repeating the thermal cycling process. For the first cycle, sample C has recorded the highest value of M_p while after three completed cycles its value diminished about 100 K. In general, T Ts values of as-cast sample increased while T Ts values decreased in the heat-treated alloys, in addition after four complete cycles, the T Ts almost stabilized. According to the obtained results, it can be said that the thermal cycling with DSC could regulate the T Ts values of all cases.

The heat exchange through the heating process (or enthalpy change ΔH_{M−A}) was obtained using DSC software program, which based on the integration from austenite start to austenite finish temperature. The area under the DSC peaks represents the enthalpy change [10]:

$$\text{area} = \int_{A_p}^{A_f} \Delta H_{M−A} \, \text{d}T$$
where $dq/dt$ is the derivative of the instantaneous heat absorbed by the sample; $T$ and $t$ are the absolute temperature and time, respectively. In addition, another extensive property is entropy change ($\Delta S$) that shows the disorderness of microstructure in the alloy. For austenite transformation, $\Delta S$ can be found using the following formula [18]:

\[ \Delta H^{M\rightarrow A} = \int_{\Lambda_1}^{\Lambda_2} \frac{dq}{dT} \left( \frac{dT}{dt} \right)^{-1} dT \]
where $T_o$ is defined as the equilibrium temperature when Gibbs free energy ($\Delta G$) in both forward and reverse phase transformation are equal to zero. The value of $T_o$ has proposed such that [19, 20]:

$$T_o = \frac{M_s + A_f}{2}$$

The value of $\Delta G$ can be found by subtracting Gibbs free energy of austenite ($G^A$) and martensite ($G^M$) at $T_o$ which is given by [21]:

$$\Delta G = \int_{A_f}^{A_i} \frac{dQ^M}{T_o} = \frac{\Delta H^{M\rightarrow A}}{T_o}$$
where \( H^A \) and \( S^A \) are enthalpy and entropy in austenite; \( H^M \) and \( S^M \) are enthalpy and entropy in the martensite phase. The pushing force for transforming austenite to martensite can be given as [22]:

\[
\Delta G^{M\rightarrow A}(T_e) = G^A(T_e) - G^M(T_e) = (H^A - T_e S^A) - (H^M - T_e S^M)
\]

\[
= \Delta H^{M\rightarrow A} - (T_e \Delta S^{M\rightarrow A}) = 0
\]

(4)

In addition, elastic energy can be obtained from the differences between Gibbs free energy at the beginning of the martensite phase transformation and when the transformation is completed [23]:

\[
\Delta G^{A\rightarrow M}(M_f) = \Delta G^{M\rightarrow A}(T_e) - \Delta G^{M\rightarrow A}(M_s)
\]

or

\[
\Delta G^{A\rightarrow M}(M_s) = -(T_e - M_x) \Delta S^{M\rightarrow A}
\]

(6)

All calculated parameters are listed in table 2. All of the calculated parameters have been obtained using DSC measurements and the aforementioned equations. In figure 4 it can be seen that all parameters have the same pattern since they are directly function of enthalpy change. Generally, the heat-treated sample at 673 K has recorded the highest value of enthalpy/entropy change with a comparably big \( \Delta G^{A\rightarrow M} \) and \( G_e \) value.

### 3.2. Crystal and microstructural analysis

Figure 5 reveals the XRD pattern of all specimens. The peaks were indexed by literature [3, 24–26]. The main peaks are \( \beta' \) (thin plate martensite) and \( \gamma' \) (thick plate martensite). Also, there are some austenite phases including, \( \gamma_1 \) and \( \alpha \). The DSC results support this finding. The matrix of all alloys showed martensite phases with
some trapped austenite precipitation phases. Furthermore, the pattern of the alloy has been affected by heat treatment, i.e. some peaks have been strengthened. Moreover, to obtain the grain size of the alloys, the Scherrer equation can be used, which is mostly limited to metallic and ceramic microstructures that have grains in the range of nano-scale. Paul Scherrer proposed his equation, which based on the wavelength of the incident x-ray ($\lambda = 1.5406 \text{Å}$), Braggs angle ($\theta$), shape factor ($K = 0.9$), and wideness at half maximum ($B$) of the XRD peak. Thus, the equation is as follows $[27, 28]$: 

$$D = K \lambda / (B \cos \theta)$$

(8)

Figure 6 shows the effect of thermal treatment on the grain size of the alloy. It is obviously can be seen that heat treatment enhanced the size of grains. It is proved that grain size influences the mechanical behavior of all materials $[29, 30]$. In this study, three different tests have been carried out for Vickers microhardness measurements. The standard deviation shows that there are different results obtained from various microstructures of the alloys (figure 7). Generally, it is found that the value of microhardness has been decreased

---

**Table 2.** Some calculated thermodynamic parameters for both treated and non-treated samples.

| $T_r$ (K) | $\Delta G^{A \to M}$ (J kg$^{-1}$) | $G_v$ (J kg$^{-1}$) | $\Delta S^{A \to M}$ (J kg$^{-1}$ K$^{-1}$) | $\Delta S^{M \to A}$ (J kg$^{-1}$ K$^{-1}$) |
|----------|-------------------------------|-------------------|------------------------------------------|------------------------------------------|
| as-cast  | 442                           | 351               | 667                                      | 14.7                                     |
| 673 K    | 509                           | 1569              | 190                                      | 3.2                                      | 22.4                                    |
| 873 K    | 525                           | 100               | 392                                      | 6.1                                      | 2.1                                     |
| 1073 K   | 528                           | 469               | 217                                      | 2.9                                      | 12.0                                    |
| 1273 K   | —                             | —                 | —                                        | —                                        | —                                       |

---

**Figure 4.** Some thermodynamics parameters of the CuAlNiTa alloys. (a) Enthalpy and entropy changes, (b) Gibbs free energy and elastic energy.
by increasing crystalline size. Also, microhardness depends on the heat treatment temperature. Sugimoto et al showed that microhardness in Cu–Al–Ni–Ti alloy starts to increase for heat treatment at 773 K, however, it falls down for higher temperatures [31]. The same results have obtained for Cu–Al–Ni–Ta alloy. On the other hand, Sampath [32] tried to enhance shape memory characteristics and ductility of CuAlNi-based SMAs through grain

Figure 5. XRD pattern of all specimens.

Figure 6. The calculated grain size of heat-treated Cu$_{83}$Al$_{13}$Ni$_{4}$ (wt%) alloy.
refinement by adding fourth elements. He found that the microhardness was increased by decreasing the grain size of the alloys [32].

The microstructure of the as-cast and heat-treated samples is shown in figure 8. There are two different martensite phases can be seen in the SEM images, where the first one is coarse-γ′, and the second one is fine β′. Also, there are some precipitation phases such as sphere-like Ta, Al, and Ta(Cu, Al) phases. Since the SEM images, has been taken in room temperature, they show γ′ and β′ phases in the matrix of all specimens, so the results support the DSC measurements which illustrate that the samples have martensite phase at room temperature. It is proved that γ′ (2 H) has higher Al content compared to β′ (18 R) phase [33]. In addition, the amount of these types of martensite phases can influence transformation characteristics such as PTTs [34, 35]. Although in the microstructure of CuAlNiTa alloy, which has been heat treated at 1273 K, shows martensite phases, there is no sign of phase transformation in its DSC measurement. In figure 8 grain boundaries cannot be seen on the given scale, while Sari [33] found that as-cast CuAlNi and CuAlNiMn alloys have shown microscopic grain about 1400 and 350 μm, respectively. The production technique is an important parameter that affects the grain size and hence all mechanical properties.

4. Conclusions

In summary, the main outcomes of this study are as follows:

- Martensitic phase transformation was observed in all heat treatment temperatures, while the sample that heat treated at 1273 K gave no result. The PTTs were increased by applying heat treatment.
- It is found that thermal cycling diminished M_p temperature in all heat-treated samples, while its value gradually increased in the as-cast alloy. The transformation temperature remains almost constant after the 3rd cycle, i.e., the thermal stability of the alloys increases.
- The XRD has shown various patterns after the heat treatment process was carried out. As the crystallization of the alloy increased, the number of diffraction peaks are also increased.
- The calculated grain size using Scherrer formula showed that the grain sizes are in the range of nanoscale, and the grain boundary cannot visible in the SEM images with Mag = 2.50 kx and 500 kx. However, the crystal size is generally increased by increasing the heat treatment temperature.
- The grain size grew up with applying the heat-treatment process. It is obtained that the quantitative value of hardness has been decreased by increasing the crystal size.
From SEM microimages and EDX analysis, it is found that there are two martensite phases in the alloys, including thin- $\beta_1$ (the matrix) and thick- $\gamma_1$ phase. In connection with the production method, Tantalum-rich regions have been found.

**Figure 8.** The SEM microimages with indicated phases.

- From SEM microimages and EDX analysis, it is found that there are two martensite phases in the alloys, including thin- $\beta_1$ (the matrix) and thick- $\gamma_1$ phase. In connection with the production method, Tantalum-rich regions have been found.
Acknowledgments

This research is supported by Firat University Scientific Research Projects Management Unit (FÜBAP, Project No: FF19.08).

ORCID iDs

Mediha Kök  https://orcid.org/0000-0001-7404-4311
Ibrahim Nazem Qader  https://orcid.org/0000-0003-1167-3799

References

[1] Lagoudas D C 2008 Shape Memory Alloys: Modeling and Engineering Applications. (Berlin: Springer)
[2] Shuntcev A, Tong Y and Li L 2019 Indentation size effect and strain rate sensitivity of Ni–Ta high temperature shape memory alloy Vacuum 160 25–30
[3] Qader I N, Kök M and Dağdelen F 2019 Effect of heat treatment on thermodynamics parameters, crystal and microstructure of (Cu–Al–Ni–Hf) shape memory alloy Physica B 553 1–5
[4] Qader I N et al 2019 A review of smart materials: researches and applications El-Cezeri Journal of Science and Engineering 6 755–88
[5] Van Humbeck J 2012 Shape memory alloys with high transformation temperatures Mater. Res. Bull. 47 2966–8
[6] Ercan E, Dağdelen F and Qader I 2019 Effect of tantalum contents on transformation temperatures, thermal behaviors and microstructure of CuAlTa HTSMA J. Therm. Anal. Calorim. 1–8
[7] Kök M et al 2018 Examination of phase changes in the CuAl high-temperature shape memory alloy with the addition of a third element J. Therm. Anal. Calorim. 133 845–50
[8] Zak G, Kneisl A and Zatulskij G 1996 Shape memory effect in cryogenic Cu–Al–Mn alloys Scr. Mater. 34 363–67
[9] Perez-Landazabal I et al 2006 Study of the stability and decomposition process of the β phase in Cu–Al–Ni shape memory alloys Materials Science and Engineering 54 734–7
[10] Recarte V et al 2004 Thermodynamics of thermally induced martensitic transformations in Cu–Al–Ni shape memory alloys Acta Mater. 52 3941–8
[11] Saud S N et al 2017 Effect of Ta additions on the microstructure, damping, and shape memory behaviour of prealloyed Cu–Al–Ni shape memory alloys Scanning 66 66–72
[12] Aydoğdu Y et al 2014 Thermal properties, microstructure and microhardness of Cu–Al–Co shape memory alloy system Trans. Indian Inst. Met. 67 595–600
[13] Dağdelen F et al 2019 Influence of Ni addition and heat treatment on phase transformation temperatures and microstructures of a ternary CuAlCr alloy The European Physical Journal Plus 134 66
[14] Deniz Çirak Z, Kök M and Aydoğdu Y 2018 The effect of chromium addition on physical properties of Cu–Al based high temperature shape memory alloy Arch. Metall. Mater. 63 1595–98
[15] Soliman H and Habib N 2014 Effect of ageing treatment on hardness of Cu–12.5 wt% Al shape memory alloy Indian J. Phys. 88 803–12
[16] Aghili M and Pelegripa J 2003 Ageing of martensite: stabilisation and ferroelasticity in Cu-based shape memory alloys Materials Science and Engineering 356 298–311
[17] Agrawal A and Dubé R K 2018 Methods of fabricating Cu–Al–Ni shape memory alloys J. Alloys Compd. 750 335–47
[18] Elrasasi T et al 2013 Effect of thermal and mechanical cycling on the elastic and dissipative energy in CuAl (11.5 wt%) Ni (5.0 wt%) shape memory alloy J. Alloys Compd. 577 5517–20
[19] Ortin J and Planes A 1988 Thermodynamic analysis of thermal measurements in thermoelastic martensitic transformations Acta Metall. 36 1873–89
[20] Kök M et al 2019 The effects of cobalt elements addition on Ti2Ni phases, thermodynamics parameters, crystal structure and transformation temperature of NiTi shape memory alloys The European Physical Journal Plus 134 197
[21] Dağdelen F, Kök M and Qader I 2019 Effects of Ta content on thermodynamic properties and transformation temperatures of shape memory NiTi alloy Met. Mater. Int. 1–8
[22] Dağdelen F et al 2003 Effects of thermal treatments on behaviour transformation in shape memory alloy Cu–Al–Ni alloys Mater. Lett. 57 1079–85
[23] Kök M et al 2019 Effects of heat treatment temperatures on phase transformation, thermodynamical parameters, crystal microstructure, and electrical resistivity of NiTiV shape memory alloy J. Therm. Anal. Calorim. (https://doi.org/10.1007/s10973-019-08788-3)
[24] Saud S N et al 2014 Effects of Mn additions on the structure, mechanical properties, and corrosion behavior of Cu–Al–Ni shape memory alloys J. Mater. Eng. Perform. 23 5620–9
[25] Saud S N et al 2015 Thermal aging behavior in Cu–Al–Ni–xCo shape memory alloys J. Therm. Anal. Calorim. 119 1273–84
[26] Cüre Y et al 2010 Evaluation of grain refiners influence on the mechanical properties in a CuAlBe shape memory alloy by ultrasonic and mechanical tensile testing Mater. Des. 31 3275–81
[27] Sugimoto K et al 1982 Grain-refinement and the related phenomena in quaternary Cu–Al–Ni–Ti shape memory alloys Le Journal de Physique Colloques 43 C4–761–C4–766
[28] Sampath V 2005 Studies on the effect of grain refinement and thermal processing on shape memory characteristics of Cu–Al–Ni alloys Smart Mater. Struct. 14 S253
[33] Sari U 2010 Influences of 2.5 wt% Mn addition on the microstructure and mechanical properties of Cu–Al–Ni shape memory alloys
Int. J. Miner. Metall. Mater. 17 192–8

[34] Sari U and Aksoy I 2006 Electron microscopy study of 2H and 18R martensites in Cu–11.92 wt% Al–3.78 wt% Ni shape memory alloy
J. Alloys Compd. 417 138–42

[35] Sugimoto S et al 1995 The effect of grain constraint, heat treatment and compositional change on the behavior of martensitic transformations in alloys with the composition near Cu–13Al–4Ni–1Zn (mass%) J. Phys. IV 5 C8-925–30