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Kinetic and structural study on CuAlMnNi shape memory alloy with a novel composition

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Abstract

In this work, a CuAlMnNi shape memory alloy with a novel composition was fabricated as cast ingot by arc melting process under vacuum. The specimens of the alloy were prepared by cutting the casted ingot alloy into small pieces. After then, all of the alloy samples were homogenized in high temperature β-phase region and then rapidly cooled by quenching them in iced-brine water in order to form martensite structure i.e., to bring shape memory property to the alloy. Then a batch of thermal and structural tests was carried out in order to probe shape memory effect characteristics of the CuAlMnNi alloy. By the differential scanning calorimetry (DSC) tests which were taken back-to-back at varied heating/cooling rates, the solid-solid martensitic phase transformation peaks that appeared on the DSC thermograms of the alloy during cyclic heating and cooling processes of the alloy were observed as an evidence for the entity of the shape memory effect property that exists in the alloy. The transformation temperatures of the alloy were slightly changed with the heating/cooling rate changed. By making DSC peak analyses, it is determined that the martensite and austenite phases averagely start to form at ~36 °C and ~64 °C, respectively. Some other transformational kinetic parameters of the alloy were also calculated. Moreover, an Af temperature lag occurred at the high heating/cooling rate of 35 °C/min, which happened mainly because of that rapid heating rate that causes the temperature signal of the DSC pan hits to the DSC detector before the signal of the alloy sample in the pan does. The differential thermal analysis (DTA) test that was run at a single heating rate demonstrated that the thermal responsive behavior of the alloy in the high temperature β-phase region matched the common behavior of Cu-Al based memory alloys. By performing room temperature EDS analysis, the composition of the alloy was determined. The X-ray diffraction (XRD) test performed at room temperature showed the β1' and dominant γ1' martensite forms that formed in the alloy and this formation was theoretically also supported by calculating the average valence electron concentration per atom (e/a) value of the alloy.

1. Introduction

In the research area of shape memory alloys (SMAs), a class of smart materials family, the cost-effective Cu-based shape memory alloys (e.g., CuAlMn, CuAlNi, CuZnAl SMAs) are regarded as the second-best SMAs after the most commercial and superior but far more expensive NiTi SMAs [1-3]. Therefore, the research done to study, change or improve the SMA properties of the Cu-based SMAs is one of the crowd-pulling research subjects in the research area of SMAs.

Although Cu-based SMAs have better thermal and electrical conductivity characteristics than those NiTi ones [3, 4], they have weaker shape memory effect (SME) properties and poor thermal stability and they also suffer from their brittleness that causes problems in their cold-working processes [4-7]. There are some ways researchers use to decrease brittleness and improve ductility and shape memory properties of the binary Cu-based

alloys (especially Cu-Al). One of them is to add extra one or more alloying elements (also called as grain refining elements) such as Mn, Fe, Cr, Co, Ti, Ni, Cr, B, Mg, Ce, Be etc. [1, 2, 5, 7-9].

The chemical composition and adding elements have also strong effects on the transformation temperatures of SMAs. The transformation temperatures and transformational kinetic parameters of a SMA are exceedingly dependent on its alloying composition. Even minor changes in composition lead to large variations of transformation temperatures. The demanded transformation temperatures for different specific applications of SMAs therefore can be met by SMAs with different compositions [9].

In this work, an experimental research study on an arc melted quaternary CuAlMnNi shape memory alloy with a novel composition and transformation temperatures are presented. The shape memory properties of the produced alloy were demonstrated by performing some thermal and microstructural measurements including DSC, DTA, and XRD.

2. Method

The CuAlMnNi SMA with a novel composition of 82Cu-12.5Al-4.5Mn-1Ni wt% (or 69.65Cu-25.01Al-4.42Mn-0.92Ni at%) was fabricated by arc melting method under argon plasma. At the beginning of the fabrication process, at first, the high purity (%99.99) metal elements of Cu, Al, Mn, and Ni powders were mixed, and then the powder mixture was pelletized under pressure. The obtained small pellets were together melted in arc melter and the as cast ingot alloy was obtained. Then small alloy samples proper for the measurements were prepared by cutting this ingot alloy. To install shape memory effect property into the alloy samples, all of them were together heat-treated in a furnace at 900 °C for 1 h for crystallographic homogenization, and at the end of this homogenization, they were immediately quenched in iced-brine water which is used as a frequent quenching method. By doing this rapid cooling from a high β-phase temperature region, the hypoeutectoid precipitations that would normally form by slow coolings are surpassed and therefore the martensite phase is forced to form in the alloy samples which is the base of shape memory properties. By using a Shimadzu 60A label DSC equipment, the DSC tests were taken under 10, 15, 20, 25 and 30 °C/min of heating/cooling rates between room temperature and 150 °C under a constant argon gas flow of 100 ml/min. The DTA test was performed under the same gas flow at a single 25 °C/min of heating rate from room temperature to 900 °C by using a Shimadzu DTG-60AH instrument. A Zeiss Evo MA10 model EDX instrument was used to determine the alloy composition under room conditions. The X-ray diffraction (XRD) test by using CuKα radiation was taken also at room temperature via using a Rigaku RadB-DMAX II diffractometer to reveal the diffraction planes of the martensite phases at room temperature.

3. Results

For all of the DSC heating/cooling rates, the multiple DSC heating/cooling running cycles of the produced CuAlMnNi SMA which were originally obtained from DSC software analysis program are presented in Figure 1. According to these DSC curves taken at different heating/cooling rates, the downward endothermic peaks seen on all heating fragments of these DSC cycles indicate the forward martensite to austenite (M→A) phase transitions, in other words, the β1' (and γ1') martensite transform into β1($L2_1$) austenite phase by the coercion of lattice internal stresses generated by heat intake (phonons) [3, 5, 10-12]. On the contrary, when looking at the exothermic peaks on the upward cooling fragments of the DSC curves, at this time the correspondent backward A→M transitions seem to have occurred. Meanwhile, on the DSC curve run at the high heating/cooling rate of 35 °C/min, an A_f temperature lag (thermal lag) [4] can be seen to have occurred in the M→A peak that appeared as a flattening in the bottom of that M→A peak. This happened mostly due to the high heating rate that leads to a delay in detection of the temperature signal comes from the alloy sample as compared to the signal comes from the DSC sample pan, the detailed reasons for this lagging temperature phenomenon is well explained in a recent work [4].

The characteristic parameters of martensitic transformation temperatures (A_s, A_f, M_s, and M_f) and enthalpy change amounts ($\Delta H_{M\rightarrow A}$) spent during M→A transformations for each heating/cooling rate were directly obtained as data sets by doing the DSC peak analyses on the DSC analyzer program which automatically uses the tangent differentiation method. Then, the values of the hysteresis gap (A_s-M_f), and the values of the other related important kinetic parameters; the equilibrium temperature (T_0), and the entropy change amounts ($\Delta S_{M\rightarrow A}$) of the CuAlMnNi SMA were calculated. All of these characteristic thermodynamical parameters with their calculated average values were listed in Table 1. Plus, the changes in the parameters of transformation temperatures, hysteresis gap, and equilibrium temperature by heating/cooling rate were drawn as line graphics and presented in Figure 2.

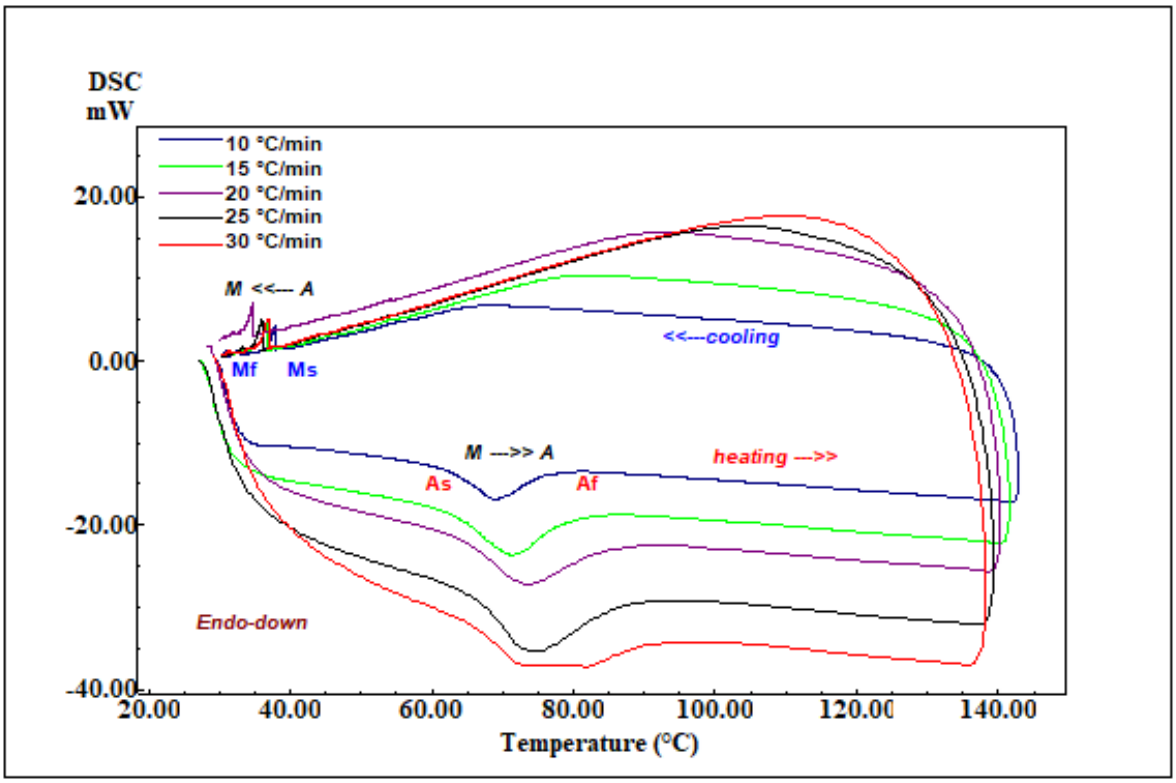

Figure 1. The multiple cyclic DSC heating/cooling curves of the produced CuAlMnNi SMA.

Table 1. The martensitic transformation temperatures and kinetic parameters of the CuAlMnNi SMA.

Heating/cooling rate (°C/min)	A_s (°C)	A_f (°C)	A_{max} (°C)	M_s (°C)	M_f (°C)	A_s-M_f (°C)	T_0 (°C)	$\Delta H_{M\rightarrow A}$ (J/g)	$\Delta S_{M\rightarrow A}$ (J/g°C)
10	62.51	76.13	69.07	37.98	36.89	25.62	57.055	6.48	0.1136
15	62.43	79.47	71.30	36.74	35.73	26.70	58.105	8.06	0.1387
20	65.48	85.52	73.58	34.75	33.93	31.55	60.135	8.68	0.1443
25	66.38	87.31	74.67	36.02	34.97	31.41	61.665	8.64	0.1401
30	66.61	93.90	81.93	36.94	35.76	30.85	65.42	7.27	0.1111
Avg.	64.20	82.11	72.16	36.37	35.38	28.82	59.24	7.965	0.1342

Among the calculated kinetic parameters, the values of equilibrium temperature (T_0) were calculated by using $\boldsymbol{T_0=(A_f+M_s)/2}$ formula [13]. The equilibrium temperature is the temperature at where the chemical free energy or the Gibbs free energy (G) amounts of both austenite and martensite phases are equalized, which means that at this point there is no driving force affecting the alloy to any transformation direction [10]. Also, the average lattice entropy change values ($\Delta S_{M\rightarrow A}$) for each endothermic M→A transformation were found by using $\boldsymbol{\Delta S_{A\leftrightarrow M}=\Delta H_{A\leftrightarrow M}/T_0}$ relation [10]. These high enthalpies and calculated entropy values mean that the CuAlMnNi alloy has a good shape memory effect.

The activation energy (E_a) parameter is also another important kinetic parameter for SMAs which is the required energy for both forward and backward martensitic transformations to occur. This energy determines the nature of the crystallization behavior of the SMAs. The values activation energy (E_a) of the CuAlMnNi alloy were computed by using the Kissinger formula [10, 14] given in Equation 1;

$$\frac{d\,[ln(\emptyset/T_m^2)]}{d(1/T_m)} = -E_a/R \qquad (1)$$

where; Φ refers to heating/cooling rate, T_m is maximum austenite peak temperature (A_{max}), R is the universal gas constant (R= 8.314 J/mol.K). The term on the left side of this equation was drawn as a plot of $ln(\Phi/T_m^2)$ versus $1000/T_m$ shown in Figure 3. This plot shows how the activation energy (E_a) changes by heating rate. By finding the slope value from applying the linear fit of this plot, and then substituting this slope value as the left term in the Equation 1, the activation energy of the alloy was calculated as 166.40 kJ/mol.

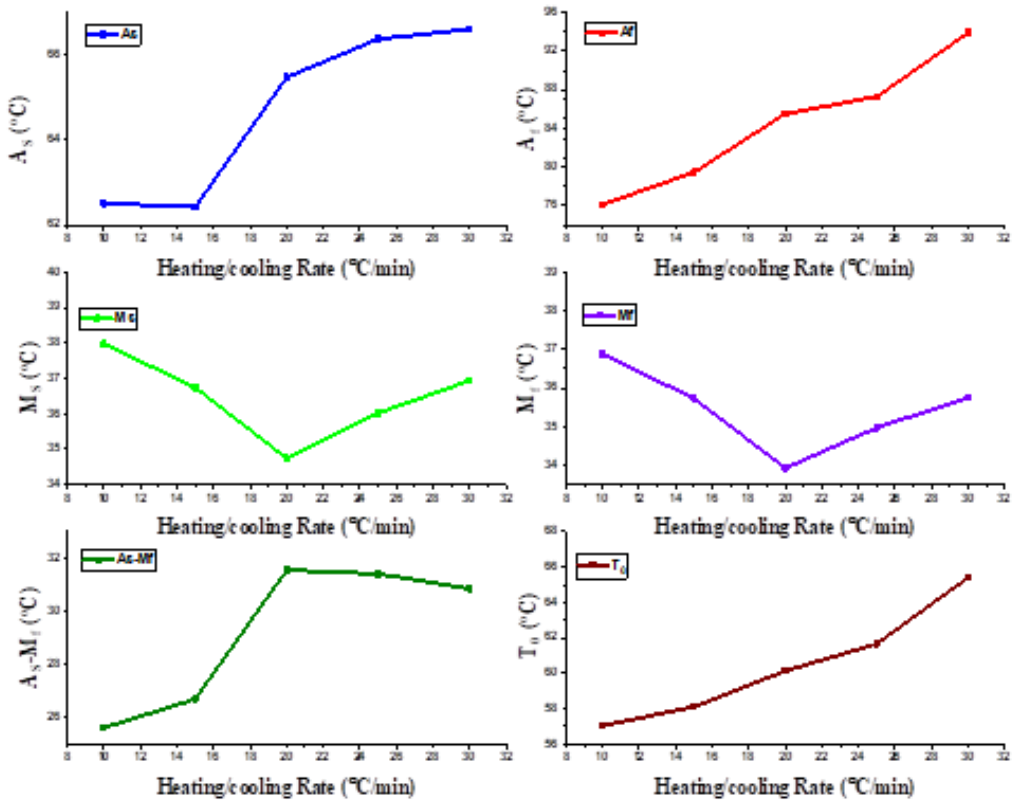

Figure 2. The graphics of characteristic martensitic transformation temperatures (A_s, A_f, M_s, and M_f), hysteresis gap (A_s-M_f), and equilibrium temperature versus heating/cooling rate.

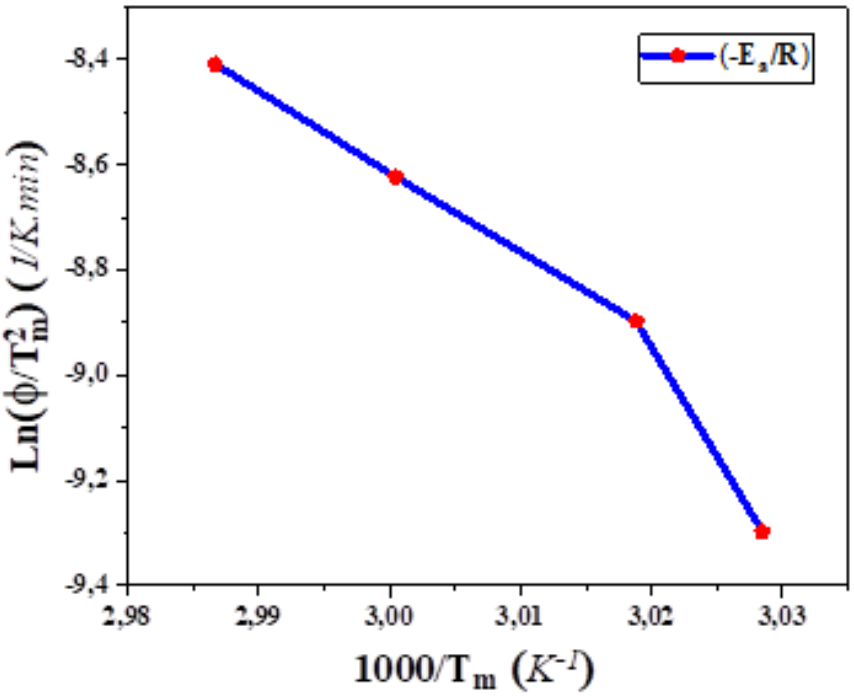

Figure 3. The graphic of the change in the activation energy E_a.

The DTA heating curve of the CuAlMnNi alloy obtained at the single heating rate of 25 °C/min is given in Figure 4. According to the appeared peaks observed on this DTA heating curve, the CuAlMnNi alloy exhibited multiple stages of phase transitions of β1'(+ γ1') → β1(DO3; L21) → β2(B2, metastable) → hypoeutectoid α+γ2 precipitations (decomposition) → eutectoid recomposition → β2(B2, ordered) → β(A2, disordered) and this common DTA pattern of Cu-based SMAs was found constant with the previous works [10, 14, 15].

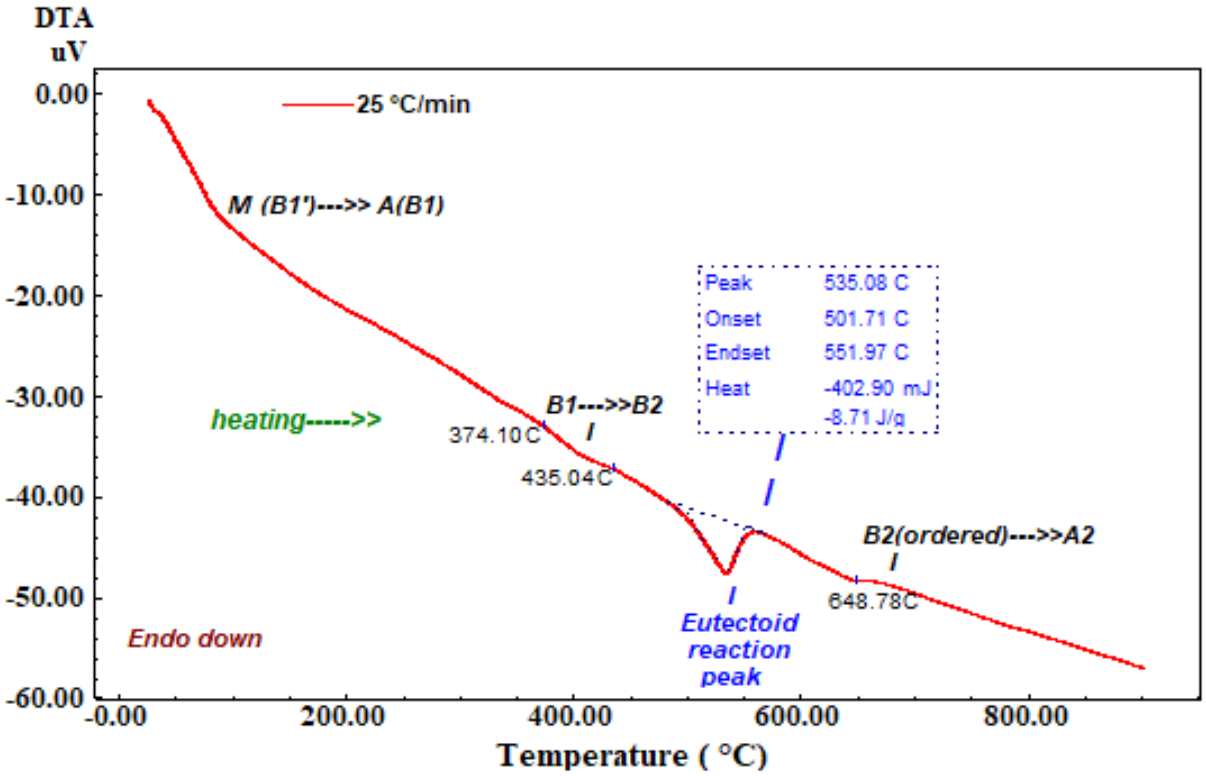

Figure 4. The DTA heating curve of the CuAlMnNi SMA, showing the sequential multiple stages of phase transitions behaviour of this alloy while it was heated through the high temperature β-phase region.

The average valence electron concentration per atom (e/a) parameter is a key parameter for Cu-based SMAs concerning having a SME property [1, 3]. The estimation on the types and volumetric dominance of the formed martensite phases in the alloy executed through this e/a parameter can give us a theoretical prediction or a prior knowledge about the martensitic nature of the alloy texture because the vibrational entropy change (ΔS) of average periodic lattice formation is a function that is highly depended on the e/a parameter [1, 3, 15]. It is expressed that the Cu-based SMAs generally must have e/a concentrations between 1.45 and 1.49 (or 1.51) to have a SME property [1, 3, 10, 15]. This e/a number value range is also a determining condition for the volumetric dominance of the monoclinic β1'(M18R) and the hexagonal γ1'(2H) types of martensite forms so that if the e/a value of a Cu-based SMA is going below this range the β1' gains dominancy over γ1', inversely as it becomes larger than this range then γ1' is the dominant martensite phase, and if the e/a value is in the mid of that range then both two types of martensite forms with nearly equal volumes take place in the alloy texture interwoven [3, 10, 15, 16]. By using the atomic fractions (f_i) of each alloying element according to the alloy composition of 69.65Cu-25.01Al-4.42Mn-0.92Ni at% and their corresponding valence electron numbers (v_i) in the $\boldsymbol{e/a=\sum f_i v_i}$ formula [10, 11] the e/a value of the produced CuAlMnNi alloy was found as 1.55, and this value indicates that the γ1'(2H) types of martensite phase must have formed in the alloy as the dominant martensite phase. This theoretical assessment or prediction on the martensitic structure of the alloy is to be verified by the structural XRD test result given below.

The XRD result showing the peaks on the diffraction pattern of the CuAlMnNi alloy labeled with the corresponding planes of both types of martensite phases can be seen in Figure 5. On this XRD pattern, it is seen that the highest diffraction peak the plane of the γ1'(211) type martensite is the main diffraction peak, so this martensite is the dominant martensite (confirming the prediction made on the e/a value of the alloy), and the other observed martensite peaks are γ1'(111), γ1'(020), γ1'(202), β1'(020), β1'(0022), β1'(12-8), β1'(2012), β1'(1210), β1'(208), β1'(331), and β1'(042) [3, 5, 10, 17-23]. Moreover, the precipitation peaks of a Cu-α(200) and a Cu_9Al_4-γ1(444), and the austenitic $L2_1$ phase peaks of β1(200) and β1(331) were observed on the XRD pattern, too [19-23]. All of the XRD diffraction peaks on the pattern seem to be broadened and which implies that the structure of the produced CuAlMnNi alloy has a highly nano-polycrystalline nature. The observed peaks are not very high and sharp, and they broadened as some conglomerations of the smaller adjacent peaks of different planes.

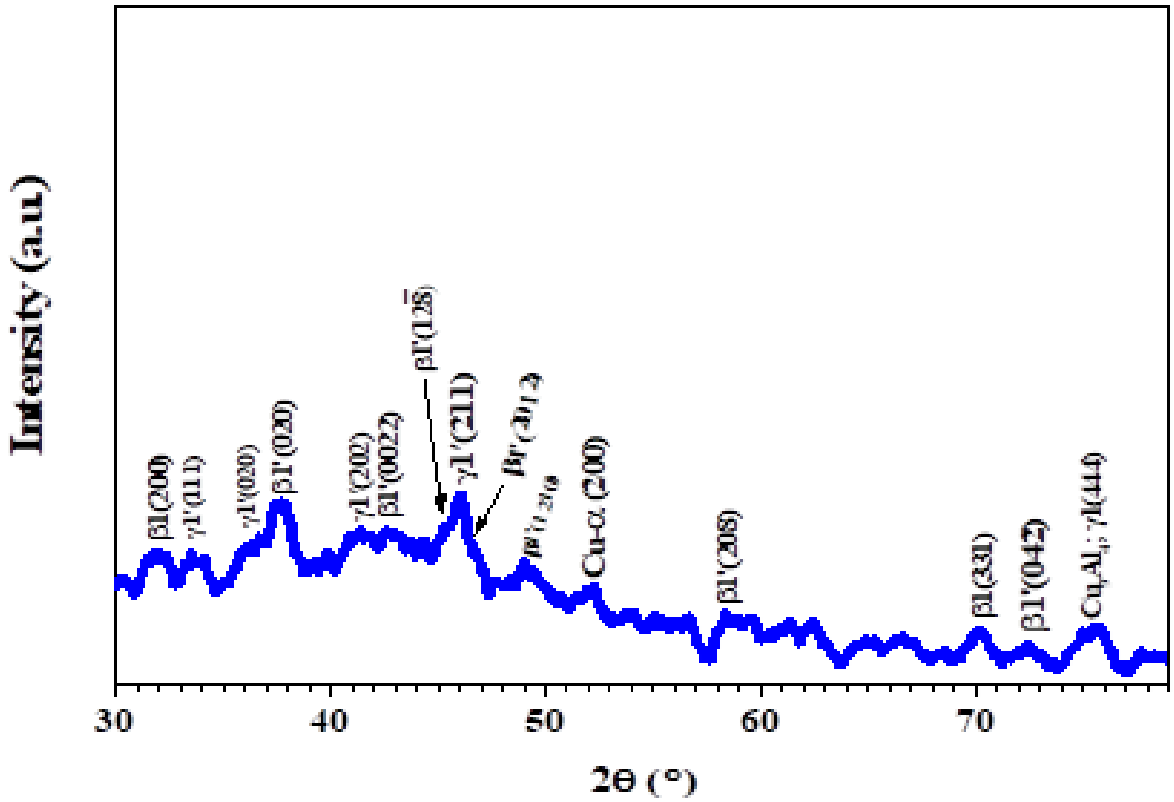

Figure 5. The XRD test result of the produced CuAlMnNi alloy. The peaks belong to the atomic planes of both types of interwoven martensite forms can be seen on this X-ray diffraction pattern.

4. Conclusion

In this work, the CuAlMnNi shape memory alloy with a new composition was successfully fabricated by the arc melting method. The alloy was characterized by thermal and structural tests that revealed the shape memory effect property of the alloy. By DSC tests the martensitic transformation temperatures and other kinetic parameters were determined. Although the transformation temperatures slightly changed at different DSC heating/cooling rates, the alloy has average M_s, and A_s temperatures of ~36 °C and ~64 °C, respectively. An A_f temperature lag was observed on the DSC curve at the highest heating/cooling rate, which happened due to this high rate. The high enthalpy and calculated entropy values indicated that the produced CuAlMnNi alloy has a good or powerful shape memory effect. The e/a valence electron concentration parameter of the alloy was determined as 1.55, which gave a pre-knowledge about the martensitic structure of the alloy predicting that there is a dominancy of martensite form over β1' martensite form at room temperature. This prediction was affirmed by the XRD pattern of the alloy showing the highest γ1'martensite peak and the other γ1' and β1' peaks. Some precipitations and austenite peaks were observed on the XRD pattern, too. The broadened and non-sharp XRD peaks indicated the highly polycrystalline texture of the produced alloy. In conclusion, this alloy with this new composition and transformation temperatures can be useful in many SMA and related applications.

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Author contributions

Oktay Karaduman: Conceptualization, Methodology, Software **İskender Özkul:** Data curation, Writing-Original draft preparation, Software, Validation. **Canan Aksu Canbay:** Visualization, Investigation, Writing-Reviewing and Editing.

Conflicts of interest

The authors declare no conflicts of interest.

References

1. Otsuka, K., & Wayman, C. (1998). Shape Memory Materials Cambridge Univ. *Press, New York*..
2. Jani, J. M., Leary, M., Subic, A., & Gibson, M. A. (2014). A review of shape memory alloy research, applications and opportunities. *Materials & Design (1980-2015), 56*, 1078-1113.
3. Canbay, C. A., & Karaduman, O. (2021). The photo response properties of shape memory alloy thin film based photodiode. *Journal of Molecular Structure, 1235*, 130263.
4. Canbay, C. A., Karaduman, O., & Özkul, İ. (2020). Lagging temperature problem in DTA/DSC measurement on investigation of NiTi SMA. *Journal of Materials Science: Materials in Electronics, 31*(16), 13284-13291.
5. Canbay, C. A., & Sampath, V. (2017). Microstructural and Thermal Investigations of Cu-Al-Mn-Ni Shape Memory Alloys. *Materials Today: Proceedings, 4*(10), 10682-10689.
6. Ahlers, M., & Pelegrina, J. (2003). Ageing of martensite: stabilisation and ferroelasticity in Cu-based shape memory alloys. *Materials Science and Engineering: A, 356*(1-2), 298-315.
7. Yang, S., Omori, T., Wang, C., Liu, Y., Nagasako, M., Ruan, J., . . . Liu, X. (2016). A jumping shape memory alloy under heat. *Scientific Reports, 6*(1), 1-6.
8. Yang, J., Wang, Q., Yin, F., Cui, C., Ji, P., & Li, B. (2016). Effects of grain refinement on the structure and properties of a CuAlMn shape memory alloy. *Materials Science and Engineering: A, 664*, 215-220.
9. Dasgupta, R. (2014). A look into Cu-based shape memory alloys: Present scenario and future prospects. *Journal of Materials Research, 29*(16), 1681.
10. Canbay, C. A., Karaduman, O., Ünlü, N., Baiz, S. A., & Özkul, İ. (2019). Heat treatment and quenching media effects on the thermodynamical, thermoelastical and structural characteristics of a new Cu-based quaternary shape memory alloy. *Composites Part B: Engineering, 174*, 106940.
11. Karaduman, O., Canbay, C. A., Özkul, İ., Baiz, S. A., & Ünlü, N. (2018). Production and characterization of ternary Heusler shape memory alloy with A new composition. *JOURNAL OF MATERIALS AND ELECTRONIC DEVICES, 1*(1), 16-19.
12. Karaduman, O., Canbay, C. A., Ünlü, N., & Özkul, İ. (2019). *Analysis of a newly composed Cu-Al-Mn SMA showing acute SME characteristics.* Paper presented at the AIP Conference Proceedings.
13. Tong, H., & Wayman, C. (1974). Characteristic temperatures and other properties of thermoelastic martensites. *Acta Metallurgica, 22*(7), 887-896.
14. Canbay, C. A., Karaduman, O., Özkul, I., & Ünlü, N. (2020). Modifying Thermal and Structural Characteristics of CuAlFeMn Shape Memory Alloy and a Hypothetical Analysis to Optimize Surface-Diffusion Annealing Temperature. *Journal of Materials Engineering and Performance, 29*(12), 7993-8005.
15. Prado, M., Decorte, P., & Lovey, F. (1995). Martensitic transformation in Cu-Mn-Al alloys. *Scripta metallurgica et materialia, 33*(6).
16. Ahlers, M. (1995). Phase stability of martensitic structures. *Le Journal de Physique IV, 5*(C8), C8-71-C78-80.
17. Braga, F. d. O., Matlakhov, A. N., Matlakhova, L. A., Monteiro, S. N., & Araújo, C. J. d. (2017). Martensitic transformation under compression of a plasma processed polycrystalline shape memory CuAlNi alloy. *Materials Research, 20*(6), 1579-1592.
18. Wee, Y., Abubakar, T., Hamzah, E., & Saud, S. N. (2015). Phase transformation and microstructure behaviour of Cu-Al-Ni shape memory alloys incorporated with cobalt addition. *Jurnal Teknologi, 74*(10).
19. Saud, S. N., Hamzah, E., Abubakar, T., & Bakhsheshi-Rad, H. (2015). Thermal aging behavior in Cu–Al–Ni–xCo shape memory alloys. *Journal of Thermal Analysis and Calorimetry, 119*(2), 1273-1284.
20. Canbay, C. A., Karaduman, O., & Özkul, İ. (2019). Investigation of varied quenching media effects on the thermodynamical and structural features of a thermally aged CuAlFeMn HTSMA. *Physica B: Condensed Matter, 557*, 117-125.
21. Yang, S., Su, Y., Wang, C., & Liu, X. (2014). Microstructure and properties of Cu–Al–Fe high-temperature shape memory alloys. *Materials Science and Engineering: B, 185*, 67-73.
22. Yang, S., Zhang, F., Wu, J., Zhang, J., Wang, C., & Liu, X. (2017). Microstructure characterization, stress–strain behavior, superelasticity and shape memory effect of Cu–Al–Mn–Cr shape memory alloys. *Journal of materials science, 52*(10), 5917-5927.
23. Karthick, S., & Palani, I. (2019). Design and development of Cu–Al–Mn shape memory alloy coated optic fiber sensor and its actuation characteristics for condition monitoring of structures. *ISSS Journal of Micro and Smart Systems, 8*(2), 89-99.