



## Influence of Heat Treatment on the Phase Transformation, Thermodynamical Parameters, Crystal Microstructure, and Of Cu-Al-X (X: Cr, Ti) Shape Memory Alloys

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### ABSTRACT

Shape memory alloys are known for their ability to return to their original shape under the influence of external factors (temperature, magnetic field and mechanical stress). Although NiTi-based alloys come to mind first when the shape memory effect is mentioned, CuAl-based alloys are very popular alternatives. The low cost of copper-based alloys is the biggest reason to study. In this study, the heat treatment effects of Cu-Al-X (X: Cr, Ti) (% weight) on some thermodynamic parameters, crystal structure and microstructure of shape memory alloy were investigated at three different temperatures (973 K, 1073 K and 1173 K). The changes in the thermal transformation of the samples were determined by Differential Scanning Calorimetry (DSC) and the changes in the crystal structure were determined by X-ray diffraction (XRD), Scanning Electron Microscope (SEM) and optical microscope device. According to DSC measurement, the temperature hysteresis of the samples decreased after the heat treatment. Besides, as the entropy change decreased, the thermal stability of the samples increased. It can be seen that the particle size of the CuAlCr alloy decreased with increasing temperature. The particle size of the CuAlTi alloy increased with increasing temperature. SEM and optical images showed that chromium (Cr) was more dissolved in the alloy compared to titanium (Ti) into CuAl alloy.

### ARTICLE INFO

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### Introduction

Shape memory alloys (SMA) have attracted attention in recent years because they are smart and functional materials [1]. SMAs are a family of smart materials that have the ability to respond instantly by changing the shapes of certain environmental stimulus species and by memorizing the initial predetermined morphology [2]. These alloys show shape memory effect (SME) and super elasticity (SE) [1]. The shape change reason of SMAs is due to diffusionless phase transformation between martensite and austenite crystal structures. This phase transformation takes place from a high symmetry austenite phase to a low symmetry martensite phase [2, 3]. Because SMAs have unique properties, they have high potential for many applications. While it is used in actuator (electrical appliances, automobile devices, robotic etc.) systems in terms of shape memory and superelastic properties, it is used in medical applications, catheters, orthodontics,

orthopedics, vascular (vessels), neurosurgery with its superelastic properties. It is also used in antennas of sensors and mobile phones [1, 4]. There are many groups of alloys that tend to exhibit SME operating at various temperature ranges. Temperature and hysteresis area are important for different application areas. HTSMAs operating at high temperatures and SMAs operating below 100 °C, known as LT SMA in the low temperature range, have wide applications in industrial and technological fields [4]. There have been extensive studies on increasing the transformation temperatures of shape memory alloys. Although the focus is on producing a Ni-Ti-based high temperature shape memory alloy, it is expensive and difficult to produce. For this reason, copper-based alloys are widely used in many areas due to their cheapness, good damping ability, high strength shape memory effect, good combination of heat and electrical conductivity [5-7]. According to Hannula, although NiTi-based SMAs are

good in recovery and superelastic properties, CuAl-based SMA's are economically suitable for work and Cu-based alloys have wider transformation temperatures, wider superelastic effects and narrow hysteresis [8-11]. V. Recarte et al. presented the effect of varying concentration of Cu-Al-Ni alloy on martensite transformation (MT) [12]. Aydoğdu et al. added Co element to the CuAl alloy and stated that it showed shape memory properties at high temperatures [13]. Addition of a third element or heat treatment to copper-based alloys improves shape memory effect, ease of fabrication, good thermal conductivity, and grain size [11, 12, 14].

Aim of this study to determine the transformation temperatures, temperature hysteresis, crystal and microstructural properties of the Cu-Al-Ti/Cr alloy by changing heat treatment temperatures. By adding third element to shape memory alloys, new shape memory alloys with desired physical properties and transformation temperature are produced.

In this direction, it is aimed to benefit in applications by adding Ti/Cr elements to the Cu-Al alloy, changing the heat treatment temperatures, determining the transformation temperatures, crystal and microstructural properties and including them in the literature.

## Experimental

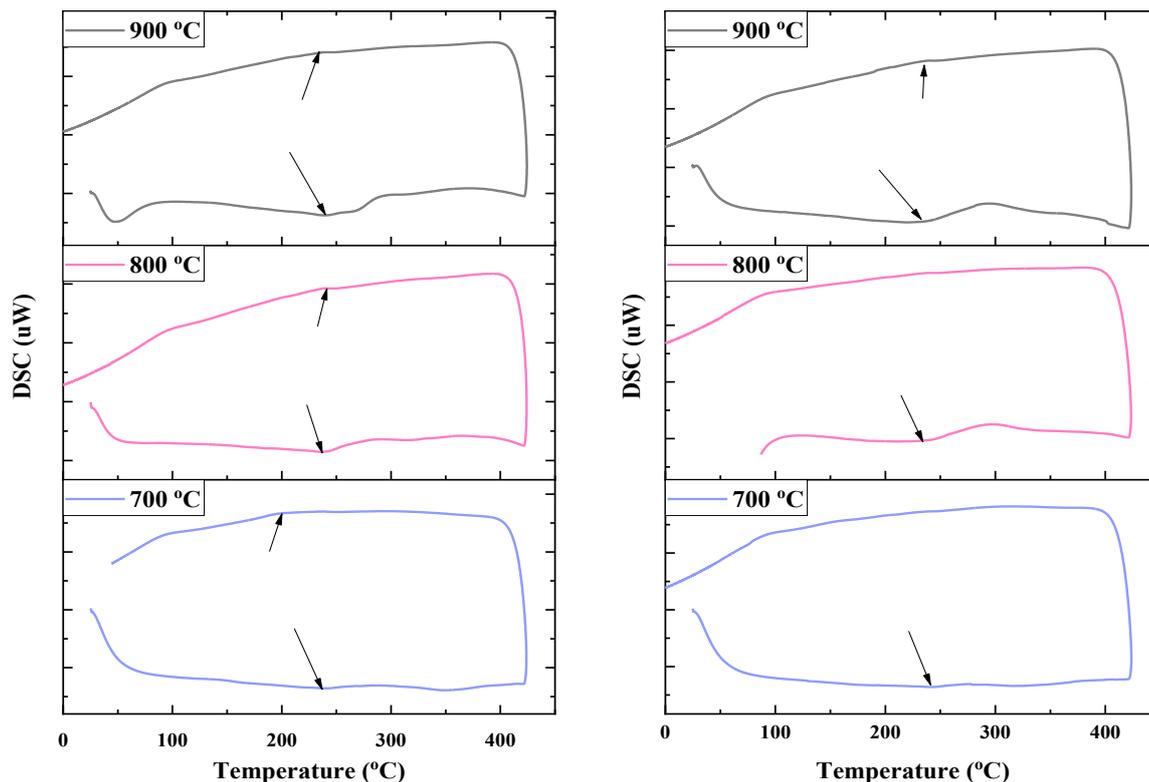


Figure 1. DSC thermograms of heat treated CuAlCr- CuAlTi alloys

X-ray measurements were taken at room temperature for the 30°–80° range (Figure 2). Two types of martensite phases peaks were observed ( $\gamma_1^1, \beta_1^1$ ) in XRD diffractograms. The obtained peaks are in agreement with the literature [6, 15, 16].  $\gamma_1^1$  phase means that thick plate martensite,  $\beta_1^1$  is sign of thin plate martensite. The particle size analysis was obtained with the Debye Scherrer

Measurement samples of  $\text{Cu}_{86}\text{Al}_{12}\text{Cr}_2$  and  $\text{Cu}_{86}\text{Al}_{12}\text{Ti}_2$  (% wt.) shape memory alloys produced by arc melting method were cut and heat treated. 700, 800 and 900 °C were chosen as heat treatment temperatures. At these temperatures, the samples were kept for 1 hour, and sudden cooling was carried out in salty ice water, and they were ready for examination. The change in transformation temperature of heat-treated CuAlCr and CuAlTi alloys was determined by differential scanning calorimetry (DSC). The effects of heat treatment on microstructure and crystal structure were determined at room temperature using x-ray measuring device, optical microscope and SEM-EDX device.

## Results and Discussions

It can be seen that DSC thermograms of heat treated CuAlCr and CuAlTi shape memory alloys in Figure 1. According to these figures, the transformation becomes more pronounced as the heat treatment temperature increases. It has been observed that the austenite-martensite transformation temperature has a very small energy at the heat treatment temperature of 700 °C. (arrow sign) It was observed that the intensity of the peaks increased and became more pronounced until the indicator of the transformation temperature at 800 °C and 900 °C. This increase is directly proportional to the heat treatment temperature.

equation based on the XRD graph and its graph was drawn (Figure 3) [17, 18]. The particle size of chromium decreased with heat treatment. On the contrary, the grain size of titanium increased with heat treatment. But the change of crystallite size of CuAlTi alloys bigger than the CuAlCr alloys.

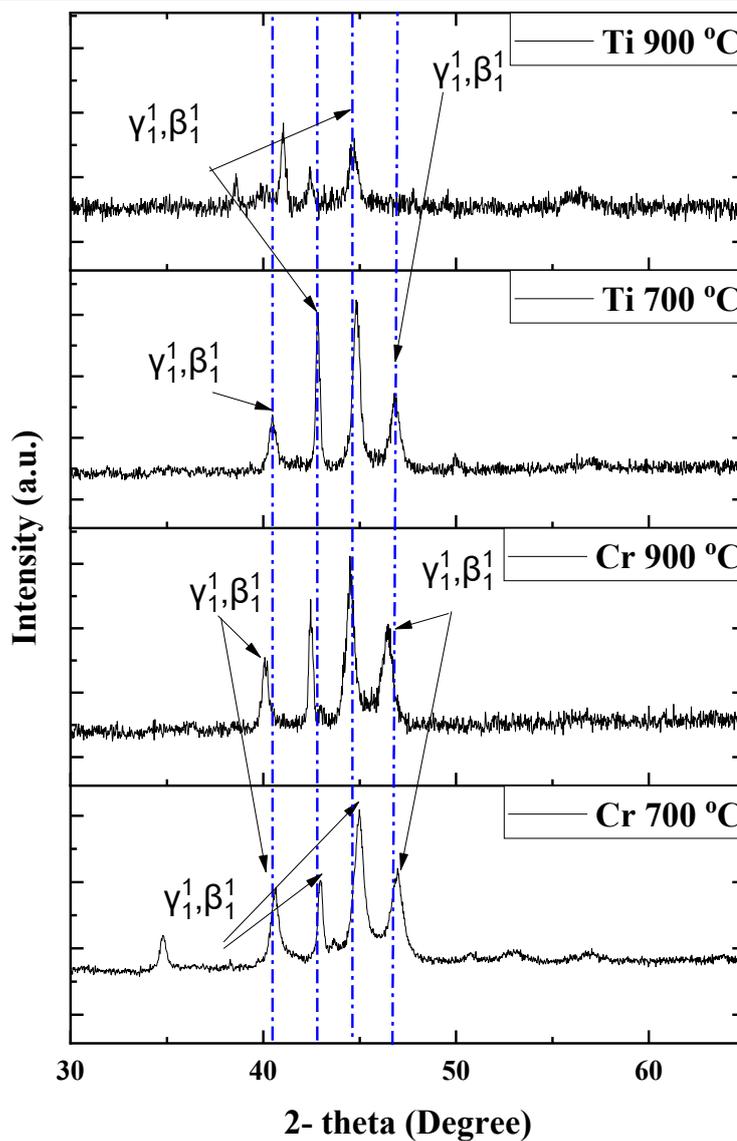


Figure 2. X-ray diffractograms of samples

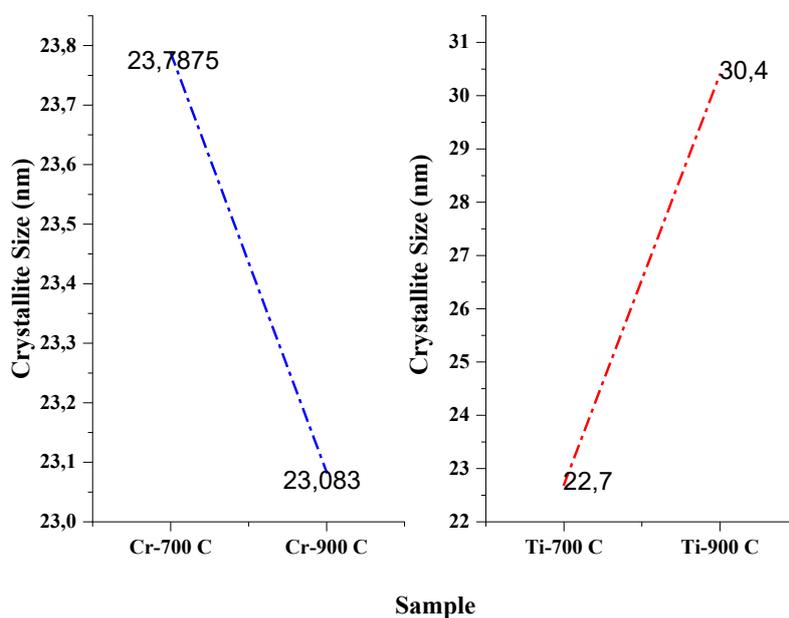
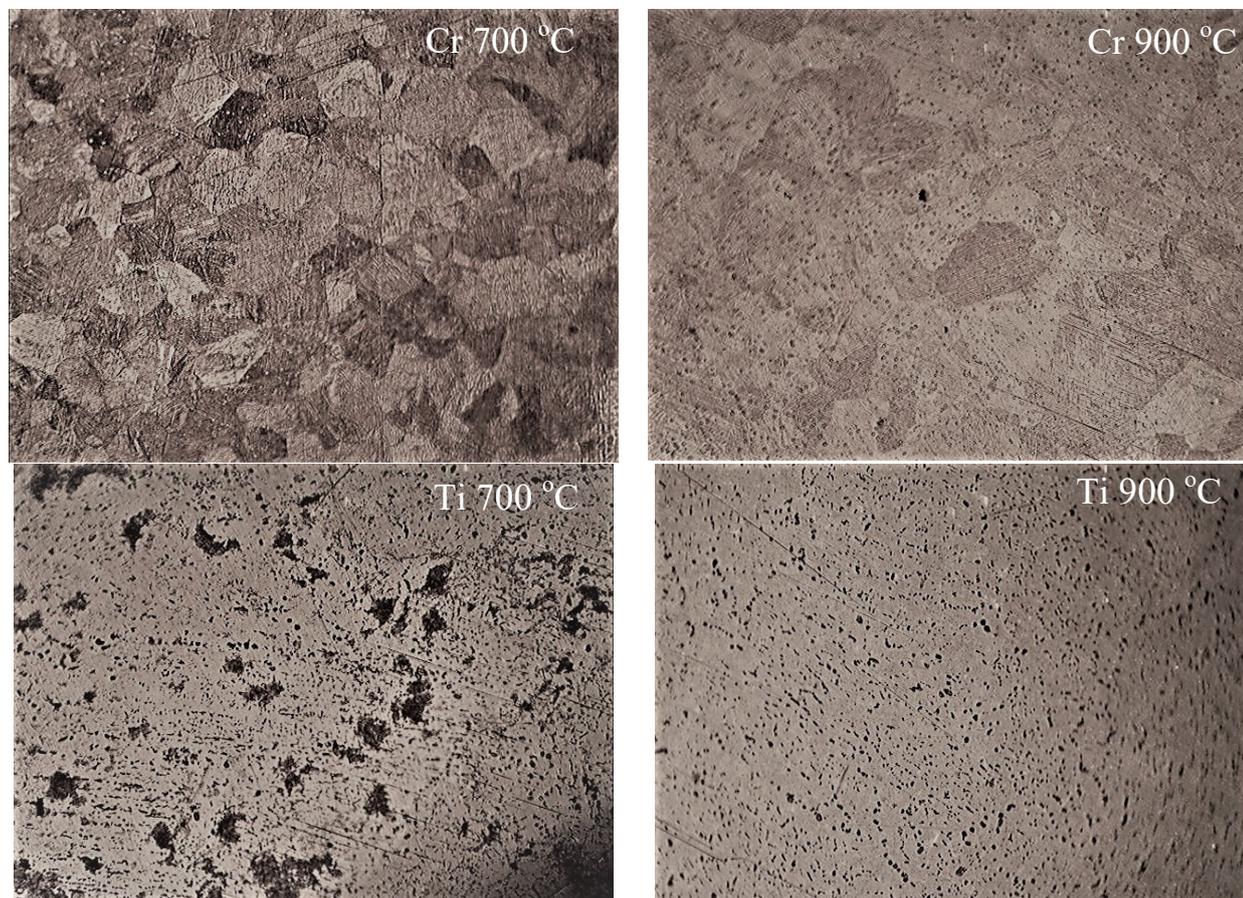


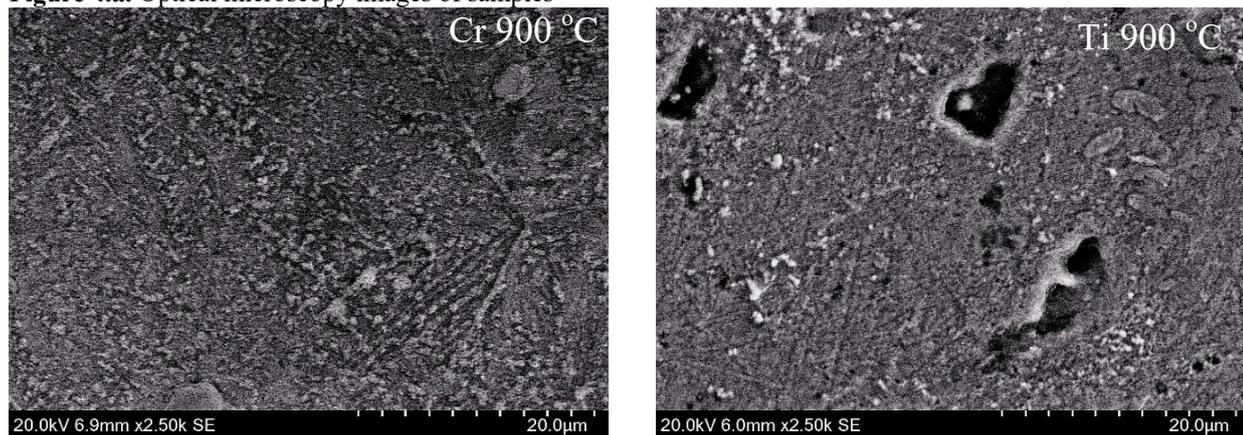
Figure 3. Crystallite size graphs of samples

In Figure 4a, optical microscope images of CuAlCr-CuAlTi alloys heat treated at 700 and 900 °C are seen. The striking point here is that grains and martensite plates are clearly visible at both heat treatment temperatures in CuAlCr alloys. In addition, the grain size increased with increasing heat treatment temperature. The reason for this rising is the increase in grain size after expansion with

temperature. For the CuAlTi alloy, the grain size was found to be too small to be seen under an optical microscope. However, martensite plates are clearly visible. SEM micrographs of both alloys heat treated at 900 °C are shown in Figure 4b. Here, thin ( $\beta_1^1$ )-coarse( $\gamma_1^1$ ) type martensite plates are clearly seen [18], while precipitate phases were also observed in the Ti-containing alloy.



**Figure 4.a.** Optical microscopy images of samples



**Figure 4.b.** SEM images of samples

## Conclusions

In conclusions, the effect of heat treatment on CuAlCr and CuAlTi shape memory alloys was investigated. As the heat treatment temperature, 700, 800 °C before the eutectic region and 900 °C after the eutectic region were selected. It was observed that the phase transformation temperatures of both alloys became more pronounced with heat

treatment and their energies increased. According to the crystal structure measurements, two different martensite phases were encountered. The  $\beta$ -phase martensite transformation is responsible for the shape memory properties of CuAl alloys. Looking at the results, thin plate  $\beta_1^1$  phase was seen. The images of the same martensite phases were also found in the microstructure measurements. When the optical microscope results were

examined, it was seen that the Cr element was better dissolved in the alloy with the increase of the heat treatment temperature. Since Cu-based alloys give the best results at 900 °C in the literature, heat treatment was applied with reference to 900 °C for SEM in the study and the plates on the surface were clearly visible. In addition, Ti precipitate phases are also observed

## References

- Otsuka, K. and X. Ren, *Recent developments in the research of shape memory alloys*. Intermetallics, 1999. 7(5): p. 511-528.
- Qader, I.N., M. Kök, and F. Dağdelen, *Effect of heat treatment on thermodynamics parameters, crystal and microstructure of (Cu-Al-Ni-Hf) shape memory alloy*. Physica B: Condensed Matter, 2019. 553: p. 1-5.
- Dasgupta, R., et al., *Effect of alloying constituents on the martensitic phase formation in some Cu-based SMAs*. Journal of Materials Research and Technology, 2014. 3(3): p. 264-273.
- Kök, M. and G. Ateş, *The effect of addition of various elements on properties of NiTi-based shape memory alloys for biomedical application*. The European Physical Journal Plus, 2017. 132(4): p. 1-6.
- Soliman, H. and N. Habib, *Effect of ageing treatment on hardness of Cu-12.5 wt% Al shape memory alloy*. Indian Journal of Physics, 2014. 88(8): p. 803-812.
- Dağdelen, F., et al., *Influence of Ni addition and heat treatment on phase transformation temperatures and microstructures of a ternary CuAlCr alloy*. The European Physical Journal Plus, 2019. 134(2): p. 1-6.
- Gustmann, T., et al., *Properties of Cu-based shape-memory alloys prepared by selective laser melting*. Shape Memory and Superelasticity, 2017. 3(1): p. 24-36.
- Hannula, S.P., et al. *Shape memory alloys for biomedical applications*. in *Advances in Science and Technology*. 2006. Trans Tech Publ.
- Alaneme, K.K. and E.A. Okotete, *Reconciling viability and cost-effective shape memory alloy options—A review of copper and iron based shape memory metallic systems*. Engineering Science and Technology, an International Journal, 2016. 19(3): p. 1582-1592.
- Saud, S.N., et al., *Influence of Silver nanoparticles addition on the phase transformation, mechanical properties and corrosion behaviour of Cu–Al–Ni shape memory alloys*. Journal of alloys and compounds, 2014. 612: p. 471-478.
- Saud, S.N., et al., *Thermal aging behavior in Cu–Al–Ni–xCo shape memory alloys*. Journal of Thermal Analysis and Calorimetry, 2015. 119(2): p. 1273-1284.
- Recarte, V., et al., *Dependence of the martensitic transformation characteristics on concentration in Cu–Al–Ni shape memory alloys*. Materials Science and Engineering: A, 1999. 273: p. 380-384.
- Aydoğdu, Y., et al., *Thermal properties, microstructure and microhardness of Cu–Al–Co shape memory alloy system*. Transactions of the Indian Institute of Metals, 2014. 67(4): p. 595-600.
- Stipcich, M. and R. Romero, *β-Phase thermal degradation in Zr-added Cu–Zn–Al shape memory alloy*. Journal of Thermal Analysis and Calorimetry, 2017. 129(1): p. 201-207.
- Kök, M., et al., *Examination of phase changes in the CuAl high-temperature shape memory alloy with the addition of a third element*. Journal of Thermal Analysis and Calorimetry, 2018. 133(2): p. 845-850.
- Chentouf, S., et al. *Stable phase formation in a 85.67 wt.% Cu-9.9 wt.% Al-4.43 wt.% Ni shape memory alloy*. in *European Symposium on Martensitic Transformations*. 2009. EDP Sciences.
- Kök, M., et al., *Effect of transition metals (Zr and Hf) on microstructure, thermodynamic parameters, electrical resistivity, and magnetization of CuAlMn-based shape memory alloy*. The European Physical Journal Plus, 2022. 137(1): p. 62.
- Kök, M., et al., *Thermal stability and some thermodynamics analysis of heat treated quaternary CuAlNiTa shape memory alloy*. Materials Research Express, 2019. 7(1): p. 015702.