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Fabrication, Phase Transformation and Microstructure Analysis of CuAlGaV Shape Memory Alloy with a Low Conduction Electron/Atom Ratio

İskender Özkul[1], Oktay Karaduman[2], Canan Aksu Canbay[3]*

[1]Department of Mechanical Engineering, Faculty of Engineering, Mersin University, Turkey
[2]Rare Earth Elements Application and Research Center, Munzur University, 62000, Tunceli, Turkey
[3]Department of Physics, Faculty of Science, Firat University, 23119 Elazig, Turkey

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Cu-based shape memory alloys (SMAs) are functional materials that exhibit shape memory effect and superelasticity due to their reversible martensitic transformation. They have attracted considerable attention for their potential applications in various fields, such as biomedical, aerospace, and automotive industries. However, there are still many challenges to overcome in order to optimize their properties and performance. In this study, we fabricated a Cu-based SMA with a new composition of CuAlGaV and investigated its phase transformation and microstructure. The alloy was prepared by using the arc melting method and then annealed at 900°C for 1 hour and cooled rapidly by quenching. The e/a ratio of the alloy was calculated as 1.33, which indicated that the alloy would most probably have a dominant β1' type and α' type of martensite phases formed by the quenching. This prediction was confirmed by the XRD analysis of the alloy, which showed that the alloy had a main peak of β1'(0018) type martensite phase and two smaller peaks of β1'(320) and α'(3R) type martensite phases. The DSC analysis revealed that the alloy exhibited a high temperature phase transformation and had a martensite stabilization, which are influenced by the alloy composition, processing, and thermal history. These results showed what thermal and structural shape memory properties the fabricated CuAlGaV alloy with low Al content exhibited.

Keywords: *CuAlGaV Shape Memory Alloy, Arc Melting, Microstructure, Phase Transformation, Low e/a ratio*

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**Corresponding author:* caksu@firat.edu.tr

1. Introduction

Shape memory alloys (SMAs) are a special class of smart materials that can recover their original shape after being deformed by external stimuli, such as temperature, stress or magnetic field [1]. SMAs have attracted considerable attention due to their unique properties, such as shape memory effect (SME), superelasticity (SE), damping and actuation capabilities [1, 2]. Among various SMAs, Cu-based alloys are of particular interest because of their low cost, wide range of phase transition temperatures and excellent functional and mechanical properties [3, 4].

However, Cu-based SMAs also face some challenges, such as poor plasticity, brittle fracture and martensite stabilization, which limit their practical applications [3]. To overcome these drawbacks, various methods have been proposed, such as adding alloying elements, inoculants, grain refinement and additive manufacturing [3].

In this study, we present a novel Cu-based SMA with low aluminum content, namely CuAlGaV quaternary alloy, which was prepared by arc melting furnance. We performed thermodynamic and structural analyses of the alloy using differential scanning calorimetry (DSC) and X-ray diffraction (XRD), respectively. To the best of our knowledge, this is the first study on the fabrication and characterization of CuAlGaV SMA by arc melting. We aim to investigate the effects of the use of the Ga and V and the low Al contents on the microstructure, phase transformation behavior of the alloy. We also compare the performance of the alloy with other Cu-based SMAs reported in the literature. The results of this study will provide new insights into the design and optimization of Cu-based SMAs for various applications.

2. Experimental

The aim of this study was to produce CuAlGaV SMA alloy by using arc melting technique. The starting materials were high-purity (%99.9) elemental metal powders of Cu, Al, Ga and V. The alloy has a nominal composition of 87.73Cu-5Al-4.7Ga-2.57V (wt.%). At first the powders were mixed and pressured into tablet forms. Then these tablets were melted in an arc melter. The arc melting process took place in a vacuum chamber filled with high-purity argon gas to avoid oxidation. The vacuum level was kept at about 7.5 x 10^{-3} Torr during the process. By this way, the as-cast ingot form of CuAlGaV alloy was obtained. Then the ingot was cut to small test samples and these samples were homogenized at 900 ºC for 1 hour and rapidly cooled by quenching them in iced-brine-water to form martensite phase in them. Differential scanning calorimetry (DSC) was used to investigate the phase transformation behavior of the CuAlGaV alloy. The DSC experiment were carried out in a temperature range between room temperature and 400 °C with a heating and cooling rate of 25 ºC /min under a constant argon gas flow. The XRD measurement for the alloy was performed by using CuKα type X-ray radiation in a a Bruker D8 Advance X-ray diffractometer.

3. Results and Discussion

In Table 1 below, the high-purity metallic elements used in the fabrication of CuAlGaV alloy are given by weight percentages. When comparing these elements, taking some factors into account is important such as valence electrons and atomic radii, there are differences between gallium (Ga) and vanadium (V) elements and the matrix element copper (Cu). The Ga element has fewer valence electrons and a larger atomic radius compared to Cu and V elements. This difference can affect the chemical reactivity and bonding properties of the Ga element. On the other hand, the V element stands out with more valence electrons and a smaller atomic radius. These factors play an important role in the alloying of the CuAlGaV alloy and in determining whether elements have similar or different chemical properties. Therefore, it can be said that factors such as valence electrons and atomic radii of alloying elements highly affect the properties of the alloy.

Table 1. The chemical compositon of the CuAlGaV alloy.

	Cu	**Al**	**Ga**	**V**
% wt.	87.73	5	4.7	2.57

The DSC result of the CuAlGaV alloy is presented in Fig.1. In some copper-based shape memory alloys, a reverse transition occurs from the martensite phase at low temperatures to austenite phase at high temperatures, but there is seen no or seen very small forward transformation from the austenite phase back to the martensite phase during cooling due to the stabilization of austenite ($L2_1$) phase [5]. This can be observed as an absence or very small DSC peak of forward austenite to martensite transformation. Similar result is observed in the DSC result of the CuAlGaV alloy, here.

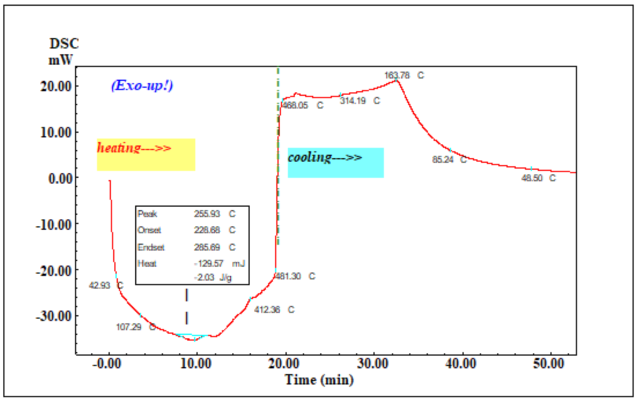

Fig.1. The DSC heating/cooling curve of CuAlGaV alloy given as on time *x*-axis.

The stabilization of austenite or martensite highly depends on the conditions of the specific composition and the processing or thermal history of the alloy and the related alloy microstructure (mainly grain size, martensite types and variants, present phases or defects) formed by depending on these conditions [5]. For instance, the addition of alloying elements such as Al, Ga, or V can enhance the stability of the martensite phase and lower the transformation temperatures [5]. Process parameters, such as cooling rate, annealing temperature and duration, and deformation, can also affect the microstructure and phase transformation of alloys [6, 7]. Indeed, the thermal history of the alloy can also influence the degree of order-disorder transition in the austenite phase, which in turn affects the nucleation and growth of martensite. The cooling rate and annealing processes, for example, can impact the formation of defects and the arrangement of atoms within the alloy's microstructure. These factors play a significant role in determining the kinetics and characteristics of martensitic transformation [5].

As seen on the heating and then cooling curve of DSC cycling (opened on the x-axis of time) of the CuAlGaV alloy in Fig.1, while the reverse martensite to austenite (M→A) transition peak is clearly seen on the left heating side, the peak of forward austenite to martensite (A→M) transition is not clearly observed or discerned (there is a little exothermic rise of A→M seen between 314 °C and 163 °C increasing toward the 163 °C but it is shallow and not seen like a peak with certain borders) due to the austenite stabilization. Which was occurred most probably due to the use of low Al content. When the DSC heating reached the high temperatures mostly some low melting point Ga diffused and played a pinning effect to hinder the L2$_1$ austenite phase transform to martensite in case of cooling. Therefore, only the M→A transformation temperatures and related enthalphy change value were determined and given in Table 2. As seen in Table 1, the fabricated CuAlGaV alloy is a high temperature shape memory alloy (HTSMA) with not a large transformation enthalpy change (ΔH) amount (ordinary CuAlMn or CuAlNi SMAs generally have higher enthalpy change values like around 5-10 J/g), so a shape memory power proportional to this enthalpy due to low Al use (because in ordinary CuAlMn or CuAlNi SMAs the Al content is about 8-14 wt.% to obtain a moderate or good shape memory property) [5].

Table 2. The transformational temperatures and enthalpy change values of M→A phase transition in SMAs.

Heating /cooling rate (°C/min)	**A_s (°C)**	**A_f (°C)**	**A_{max} (°C)**	**$\Delta H_{M\rightarrow A}$ (J/g)**
25	228.68	285.69	255.93	2.03

The average conduction (valence) number per atom ratio (e/a ratio) of the fabricated CuAlGaV alloy was determined as 1.33 by using $e/a=\sum f_i v_i$ formula [8]. Where; f_i represents the atomic percentages of the alloying elements in the alloying composition of the CuAlGaV alloy (its atomic composition is 81.994Cu-11.006Al-4.004Ga-2.996V at.% which corresponds to its mass composition 87.73Cu-5Al-4.7Ga-2.57V wt.%), and v_i is the valence number of these elements (these are $v_{Cu}=1$, $v_{Al}=3$, $v_{Ga}=3$, and $v_V=2$). The e/a ratio of an alloy is a key parameter for Cu-based SMAs in order to have a shape memory effect property [8, 9]. It is also a theoretical predictor for the existence, type and volumetric dominancies of martensite phases formed in a Cu-based SMA. Cu-based shape memory alloys with e/a ratio values within or close to the e/a ratio range between 1.45-1.51 theoretically can show a shape memory effect [8, 9]. Moreover, within this range β1' and γ1' type martensites are co-existed nearly equi-volumetrical, and as descending below this range β1' gains dominancy over γ1', and vice-versa above the range [8, 9]. So, the calculated e/a ratio (1.33) here for the fabricated CuAlGaV alloy is found as below this range and therefore the β1' martensite is expected to be formed highly dominant in the CuAlGaV alloy. As a matter of fact, this expectancy is rewarded by the below given result of XRD measurement performed at room temperature, i.e., when CuAlGaV alloy was in martensite phase.

The XRD result of the fabricated CuAlGaV alloy is presented in Fig.1. The highest intensity (main) peak emerged at the angle of 2θ=42.989 on this X-ray diffraction pattern of the alloy indicates β1'(0018) type martensite phase, and the other two observed peaks respectively from left to the right indicate a Cu-α(200) phase and the peak of β1'(320) and α1'(3R) which were determined according to the literature [10-12]. Here, it is seen that there is no any γ1' type martensite peak emerged (or can not be clearly observed) on the pattern due to the use of low Al content which led the produced CuAlGaV alloy to have an e/a ratio value below than the above-mentioned e/a ratio range of 1.45-1.51. So, only the β1' type (also a lesser α1' type) martensite is seem as been formed in the CuAlGaV alloy and this meets or confirms that expectancy mentioned above. Also, this result is found compatible with the DSC result of the CuAlGaV alloy. The low Al content fully used in formation of L2$_1$ austenite phase which normally (if not hindered) transforms fully into β1' martensite by cooling, and some regions without Al atoms in the CuAlGaV alloy matrix became an intermetallic phase which is the Cu-rich α-phase observed on the XRD pattern. Also, large plates of α′ type martensite will be formed, if the Al percentage is less than 11.9 wt.% [13].

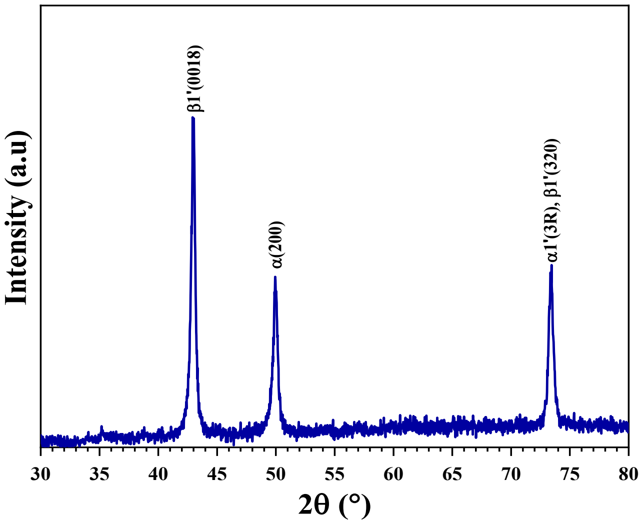

Fig.3. The X-ray diffraction pattern of the CuAlGaV alloy.

The average crystallite size (D) value of the CuAlGaV alloy was calculated by using the famous Debye-Scherrer formula [8] given as below;

$$D = \frac{0.9\lambda}{B_{1/2} cos\theta} \qquad (1)$$

where; λ is the wavelength of the CuKα type X-ray radiation (λ=0.15406 nm), θ is the Bragg angle of the diffraction and B1/2 is the full width at half maximum (FWHM) value of the maximum intensity peak (the main peak). The average crystallite size D value of the CuAlGaV alloy was found as 24.09 nm and this value is found in good concordance with the literature values [8, 14, 15].

4. Conclusions

The aim of this study was to fabricate a CuAlGaV alloy and to examine its phase transformation and microstructure characteristics related to its shape memory properties. The alloy was prepared by using the arc melting method and then annealed at 900°C for 1 hour and quenched. The alloy composition, processing, and thermal history were expected to affect the stability of the austenite and martensite phase and the phase transformation in the alloy. The DSC analysis revealed that the alloy had a stability of the austenite phase, which was mostly attributed to the pinning effect of low melting point Ga content which some diffused during the DSC heating process. The e/a ratio of the alloy was found as 1.33 due to the low content of Al element, which indicated that the alloy would have a dominant β1' martensite phase expected to be observed at room temperature. This prediction was confirmed by the XRD analysis, which showed that the alloy had a main peak of β1'(0018) type martensite phase and two minor peaks of β1'(320) and α1'(3R) type martensite phases as expected due to the low Al use.

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