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Effect of Ag Nanoparticles Addition on the Microstructure of Cu-21%Zn-6%Al Shape Memory Alloys

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Abstract

This paper aims to investigate the effect of Ag nanoparticles addition in different percentages (0.12 wt. %, 0.15 wt. %, 0.25 wt. %, 0.35 wt. %) on the microstructure properties of Cu-21%Zn-6%Al shape memory alloy. Optical and SEM were carried out to studied such effects. Two heat treatments were carried out at (825 ℃ and 850 ℃) for 10 min and quenched in ice water. It was observed that both of heat treatment lead to formation M18R martensite with V-shape and needle like, but raising the temperature of heat treatment from 825 ℃ to 850 ℃ lead to a decrease formation α phase, which leads to improving the shape memory properties. Refinement of the grain size resulted as Ag nanoparticles addition increased from 0 to 0.25 wt. %, the grain size decreases from 1551 μm to 212 μm with reduction of 86.32 wt. % at 0.25 wt. % Ag. The microstructure observation indicated that the Ag nanoparticles addition leads to creating a multi-variant oriented martensite microstructure after quenching process in ice water.

Keywords: Nanoparticles, SMA, Martensite, Cu-Zn-Al system.

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1. Introduction

Shape memory alloys (SMAs) have a special feature related to the reversible phase transition from martensite to austenite. Through the application of heat, it is possible to restore their original shape after plastic deformation [1]. Currently, Ni-Ti alloys and Cu-based alloys are the most studied alloys and the materials that offer SME. However, Cu-based alloys are a great alternative for Ni-Ti SMA due to they are less costly and have higher electrical and thermal conductivities [2]. The demand for shape memory alloys has increased due to their special properties and various uses, such as actuators, vibration-dampers, structural connectors, manipulators in the aerospace and automotive application [3], [4]. Cu-Zn-Al alloy has great attention in the last decade due to low cost, availability in the market, good electrical and thermal conductivity, superior strain

Recovery compared to another Cu-based alloy (SMA), and relative ease of fabrication. The disadvantage of Cu-Zn-Al alloys is the martensitic stability which means an increase in the reverse transformation temperature through thermal cyclic leads to degradation of shape memory effect, poor ductility, low strength, and the intergranular crack because this alloy presents rapid grain growth during betatising treatment. Cu-Zn-Al alloys are used in a variety of products, including thermal actuators, springs, fasteners, and couplings [5]. The shape memory effect for Cu-Zn-Al alloy can be observed within a specific range of composition, generally contains (15 - 30) % of Zn and (4 - 10) % of Al. Hence, the shape memory properties depend on the composition of the alloy. Three equilibrium phases may happen (α, β, and γ) depending on the temperature and chemical composition. However, the high-temperature phase (β) with BCC structure is a particular phase that shows the shape memory effect through martensitic transformation by the cooling process. The disorder parent phase (β) transforms and order to superlattice structure β_2 (B2) and β_3 ($L21$) by the cooling process [6]. Many investigations have been made to enhance the microstructure, mechanical properties, thermal stability for the martensitic transformation, and shape recovery rate as well as prevent the intergranular crack by aging treatment and adding grain refinements such as Ti, Co, V, and Zr and another alloying element.

Han and Kim [7] have been reported a refinement in the grain size due to the effect of boron addition with 0.1 wt. % on the Cu-14.7%Zn-8.5%Al. The grain size was reduced from 2 mm to 400 μm by about 80 % at 0.1 % B. The activation energy for the alloys with boron addition was increased to 200 kJ/mol. Kim [8] have studied the effect of adding (1 Ni, 0.2 Si, 0.2 Zr, 0.2 Ti wt. %) on the Cu-24.5%Zn-4%Al alloy. Through the examination, the grain size was reduced from 1500 μm to 220 μm by about 85 % due to microalloying element addition. The microstructure of alloys with the addition of microelement consists of a mixture from M18R a type of martensite and DO_3 the parent phase also, showed the microalloying element addition lead to the refinement of martensite variants. Zou et al. [9] have observed 1 % Mn and 0.5 % Zr addition on the Cu-21%Zn-6%Al alloys provides a decrease in grain size from 300 μm to 75 μm. Xu [10] studied the effect of rare earth element (Gd) gadolinium addition on Cu-Zn-Al alloy. Reduction in the grain growth of the Cu-Zn-Al alloys due to the effect of Gd addition, which was lead to formation spherical phase from Gd-rich precipitates in the matrix, and that lead to decrease in the grain size by about 61.5 % from 520 µm to 200 µm at 0.08 % wt. Gd. The shape recovery rate and mechanical properties of Cu-Zn-Al-Gd alloys were improved more than the base alloy. Bhuniya et al. [11] have showed effective improvement for alloys with Zr addition more than Ti addition. It has been observed the existence of a small amount of $ZrAl_3$ aging precipitates in β' phase, which leads to improve nucleation of the favorable martensite plates, also Zr addition lead to overcome the degradation of shape memory effect as a result of aging influence in Cu -Zn -Al alloys moreover, Ti presence provide a decrease in grain size more effectively than Zr by retarding the grain growth process as a result of restricting grain boundary by Cu_2AlTi precipitates. Yang et al. [12] have investigated the effect of addition mischmetal on Cu-Zn-Al alloy. It has been observed reduction from 1000 µm to 30 µm in grain size at 0.43 wt. % mischmetal. Chanmuang et al. [2] studied the influence of indium addition on the Cu-Zn-Al shape memory alloy. Cu-Zn-Al-In alloys microstructure was plate-like martensite with two types of martensite phase have been observed 2H and 18 R martensite structure, and that leads to an increase in the shape memory recovery in this alloy. The Alaneme and Umar [13] investigated the effect of adding different amount of Ni on the microstructure of Cu-Zn-Al alloy. The grain structure for the base alloy and Cu-Zn-Al-0.4%Ni alloys had elongated grain with a sharp edge, while the Cu-Zn-Al-alloy with (0.1, 0.2, 0.3 wt. % Ni) had more curved /round /granular grain edges and finer grain size, which lead to improve the mechanical properties for this alloy. The main objective of this study is to investigate the effect of Nano Ag on microstructure of the Cu-21%Zn-6%Al alloy.

2. Experimental procedure

2.1. Casting process and heat treatment

Cu-21%Zn-6%Al alloys were prepared by cutting scrap copper electric wire, aluminum wire, and anodes of pure zinc 99.9 % into small pieces and melting them in a crucible furnace with varying percentages of silver nano-powder. All of the alloys' molten mixtures were poured into a sand mold. The chemical compositions of the alloy that has been produced are showed in Table 1.

Table 1. The chemical compositions of Cu-Zn-Al-Ag SMAs.

Sample No.	Cu wt.%	Zn wt.%	Al wt.%	Ag wt.%
1	73	20.9	6.1	0
2	72.55	21.3	6.15	0.12
3	72.3	21.4	6.3	0.15
4	73.1	21.1	5.8	0.25
5	73.25	20.3	6.45	0.35

To achieved homogeneous structure for Cu-Zn-Al-Ag alloys; they were heated to 800 °C for 2 hours, and then followed by slow cooling inside a furnace. This treatment will provide enhancement for the microstructural and chemical homogeneity of the alloys [13]. The alloys then were heated to 825 °C and 850 °C for 10 min and quenched into ice water to study the microstructure of the Cu-Zn-Al alloys [14], [15].

2.2. Microstructural characterization

The microstructures specimens were prepared by cutting, grinding, and then followed by polishing according to ASTM E3 standard [16]. Subsequently, the specimens were etched in a solution of 5 g $FeCl_3$, 50 ml HCl, and 100 ml H_2O, swabbing for 2-5 s were done according to the ASTM E407 standard [17]. The microstructural examination was accomplished by using optical microscopy (OLYMPUS-Japan) and scanning electron microscopy (NOVA Nano SEM) to notice phase distribution, and the influence of Nano-Ag on the grain size of the Cu-Zn-Al alloys.

3. Results and discussion

3.1. Microstructures of the Cu-Zn-Al-Ag alloys

The optical micrographs of the Cu-Zn-Al SMA with and without Ag nanopowder as-cast were examined. The microstructure of base alloy without nano Ag has a single α (FCC) phase as shown in Fig. 1 (a), while the microstructure in the alloys with different amount of Ag has two phases $\alpha + \beta$ (FCC + BCC), which was indicated, where the white area belongs to α phase and the dark area belong to β phase as shown in Fig. 1 [18]. The β phase increases, and the α phase decreases with increasing nano-Ag addition. It can be noticed that nano Ag addition has a significant effect on grain size. In the case of base alloy, the magnitude of the grain size presents in the coarse one is about 1551 µm, but it becomes more refined with an increasing amount of Ag nanoparticles; moreover, the average size is about 212 µm with 0.25 wt. % Ag as shown in Table 2. This means nano-Ag either formed intermetallic compound or precipitated in the matrix. Thus, the grain growth velocities were restricted, and the atom in the grain boundary was hindered from migration. It is supposed intermetallic compound or precipitate of nano-Ag works as nucleation sites which finally causes the grain refinement and increase number of grains [10].

The samples were heated at two different temperatures and at the same time period (825 ℃ and 850 ℃) for 10 min to obtain the preferred properties and reach the beta phase area upon heating. Also, cooling by ice water from this temperature will lead to obtain a full martensite phase structure which is responsible for the shape memory effect [14].

The optical microstructure of Cu-Zn-Al SMA with and without Ag addition heated to 825 ℃ for 10 min then quenched in ice-water was examined. It can be observed the microstructure of the Cu-Zn-Al SMA consist of a α' martensite plate and α phase matrix structure as shown in Fig. 2 (a). The microstructure of Cu-Zn-Al SMA with 0.12 wt. % Ag consists of the dendritic α phase precipitates in β_1', the matrix is shown in Fig. 2 (b). A decrease in α phase, which was distributed in the β_1', matrix can also be observed; moreover, the martensitic plate matrix with a V-shape was formed as shown in Fig. 2 (c). The microstructure was generated and observed entirely martensite at (0.25 and 0.35 wt. %) Ag addition, as shown in Fig. 2 (d), and (e). The changing in the microstructure from α to the β_1' martensite with differently oriented variants because the Cu-base shape memory alloys were very sensitive for the adding alloying element, which are lead to altered in the temperature of the martensitic transformation [14].

The microstructure of Cu-Zn-Al SMA with and without Ag addition which was heated to 850 ℃ for 10 min, then quenched in ice-water, as shown in Fig. 3. It can be observed the microstructure of the Cu-Zn-Al SMA consist of α phase matrix with α' martensite like a thick plate with thickness reach to 1.487 µm as shown in Fig. 3 (a) and Fig. 4 (a), while the microstructure of Cu-Zn-Al SMA with 0.12 wt. % Ag consists of the α phase precipitates with (FCC) structure irregularly distributed in $\beta_1^{'}$, the matrix is shown in Fig. 3 (b) and Fig. 4(b); moreover, the martensite-like plate with 0.415 µm thickness appeared and was observed by SEM. A change in the microstructure has been observed, which was disappear for α phase and the dominance of the $\beta_1^{'}$ martensite phase over the microstructure with martensite plate thickness 0.325 µm as shown in Fig. 3 (c) and Fig. 4 (c). Fig. 3 (d) shows the microstructure of Cu-Zn-Al SMA with 0.25 wt. % Ag, which was entirely twining martensite with fine plate thickness 0.3 µm as shown in Table 2.

Fig. 3 (e) and Fig. 4 (e) show the micrographs of Cu-Zn-Al SMA with 0.35 wt. % Ag. The alloys have the same morphology mentioned previously, but with a slight increase in thickness of martensite. Also, it can be observed the martensitic plates in a V-shape in some grains and needle-like in others with several twin boundaries (TB) in the Cu-Zn-Al SMA with (0.15, 0.25, 0.35) wt. % Ag, which was generated during the martensite transformation by cooling process from the closed peaked structure of β parent phase. The self-accommodating variants with zig-zag morphology for the martensite can be observed and increased with nano Ag's addition. This morphology can be formed explicitly in the copper-based alloys. The Cu-Zn-Al alloy with (0.15, 0.25, 0.35) wt. % Ag showed a microstructure with the entire martensite and disappeared for α phase. This kind of plate and needle-like for martensite morphology for Cu-Zn-Al SMA alloy was reported [19], [20].

Table 2. The average grain size for Cu-Zn-Al as-cast alloys and the martensite plate thickness for the alloys that heated at 850 ℃ for 10 min and quenched in ice water.

Alloys	Average grain size (µm)	Martensite plate thickness (µm)
Cu-Zn-Al	1551.505	1.487
Cu-Zn-Al-0.12%Ag	264.0117	0.415
Cu-Zn-Al-0.15%Ag	248.1623	0.325
Cu-Zn-Al-0.25%Ag	212.126	0.3
Cu-Zn-Al-0.35%Ag	246.6723	0.432

By comparing between Fig. 2 (b) and Fig. 3 (b), it was noticed that the volume fraction of α phase precipitates in the $\beta_1^{'}$ phase decrease with increasing temperature of the heat treatment for Cu-Zn-Al-0.12 % Ag SMA from 825 ℃ to 850 ℃. Also, by comparing between Fig. 2 (c) and Fig. 3 (c), it was observed that the α precipitates disappeared with increasing heat treatment temperature from 825 ℃ to 850 ℃ for Cu-Zn-Al-0.15 % Ag SMA. For that reason, raising the temperature of heat treatment will lead to obtaining a $\beta_1^{'}$ martensite microstructure and decrease α phase after the cooling process and that will improve the shape memory effect because the presence of α phase leads to degradation in shape memory effect [21].

Fig. 5 illustrated the optical microstructure of Cu-Zn-Al SMA without nano-Ag addition heated to 900 ℃ for 10 min then quenched in ice-water. It can be observed the microstructure consist of (α + $\beta_1^{'}$) phase structure. By comparing between Fig. 2 (a), 3 (a) and Fig. 5, it was noticed that the first and second figure shows the alpha phase microstructure, while at the Fig. 5 it was observed the presence of ($\alpha + \beta_1^{'}$) phase microstructure. It was concluded that raising the temperature of thermal treatment to 900 ℃ leads to reach the region of (α + β) as shown in the equilibrium phase diagram for Cu-Zn-Al alloy [6]. The goal of heating was to get a β austenite region and then quenching in ice water to achieve $\beta_1^{'}$ martensite microstructure, which is responsible for the recovery mechanism.

Whereas nano-Ag addition lead to obtain $\beta_1^{'}$ martensite after heat treatment at 825 ℃ and 850 ℃, but with higher efficiency at 850 ℃, it may due to change the transformation temperature and shift the equilibrium phase diagram.

4. Conclusions

The influence of Nanosilver powder on the microstructure of the Cu-Zn-Al SMAs with 0.12-0.35 wt. % was investigated at two heat treatment temperature (825 ℃ and 850 ℃) for 10 min and quenched in ice water. The following conclusions have been reached based on the observations:

1. Nanosilver powder addition lead to decreasing the grain size from 1551 µm to 212 µm with reduction rang reach to 86.32 % at o.25 wt. % Ag.
2. Raising the temperature of heat treatment from 825 ℃ to 850 ℃ lead to a decrease formation α phase, which leads to improving the shape memory properties.
3. The microstructure of the Cu-Zn-Al-Ag alloy present the formation of M18R martensite with needle-like, and V-shape and with twining TB morphology which is essential for shape memory effect.

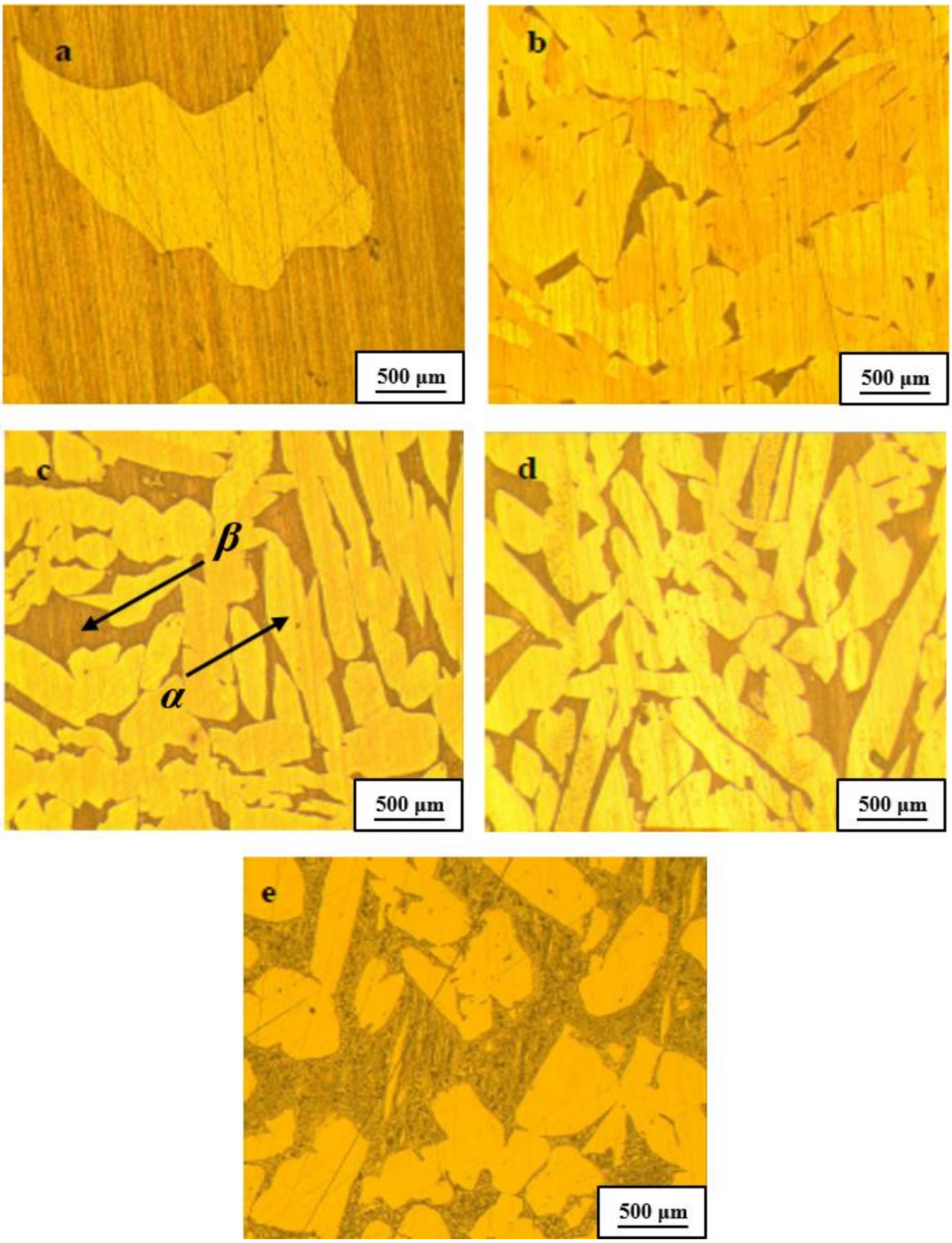

Fig. 1 Optical micrograph of Cu-Zn-Al as-cast alloy **(a)** 0 % Ag **(b)** 0.12 % Ag **(c)** 0.15 % Ag **(d)** 0.25 % Ag **(e)** 0.35 % Ag.

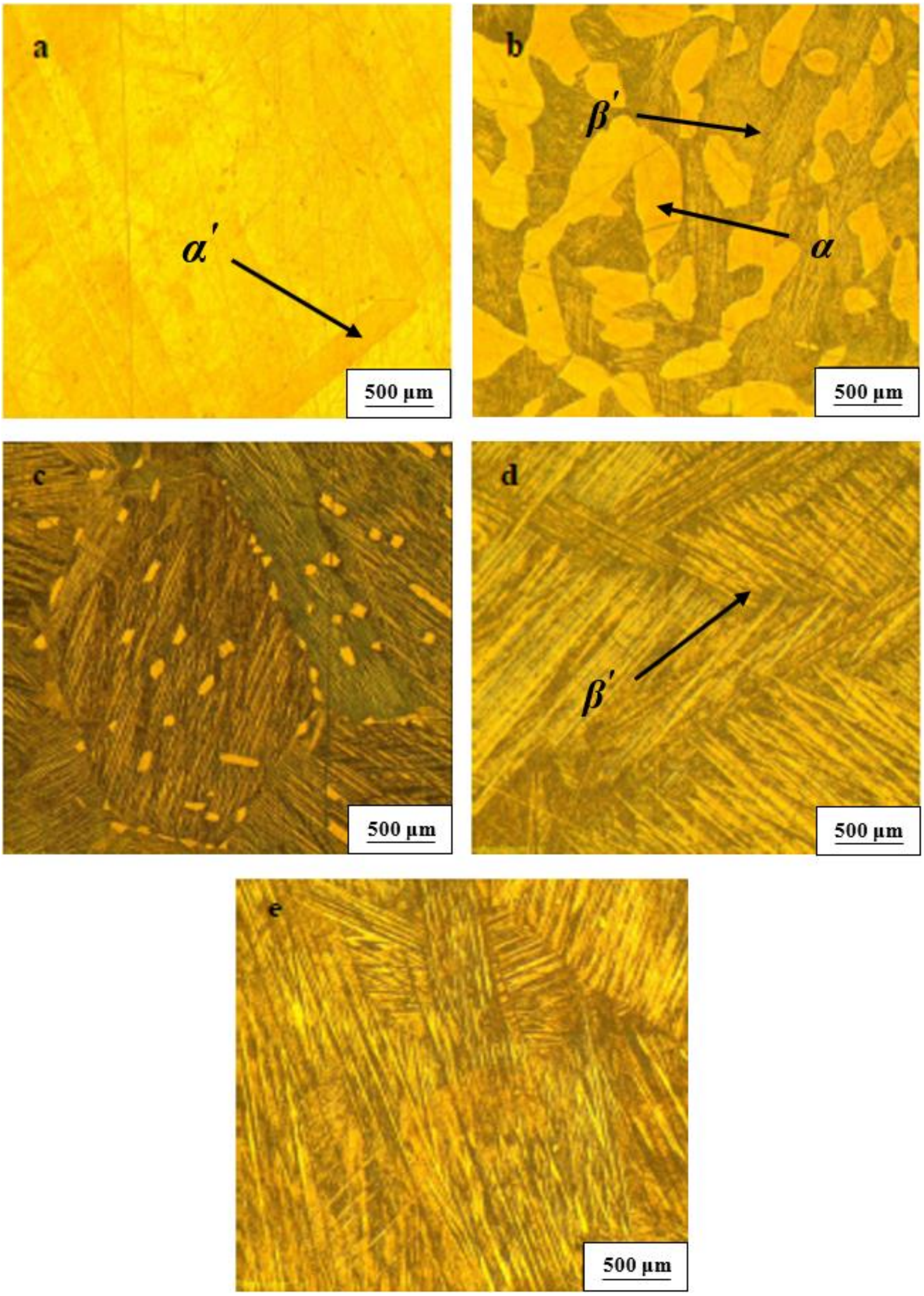

Fig. 2 Optical micrograph of Cu-Zn-Al alloy heated to 825 ℃ for 10 min and quenched in ice water, (a) 0 % Ag, **(b)** 0.12 % Ag, **(c)** 0.15 % Ag, **(d)** 0.25 % Ag, **(e)** 0.35 % Ag.

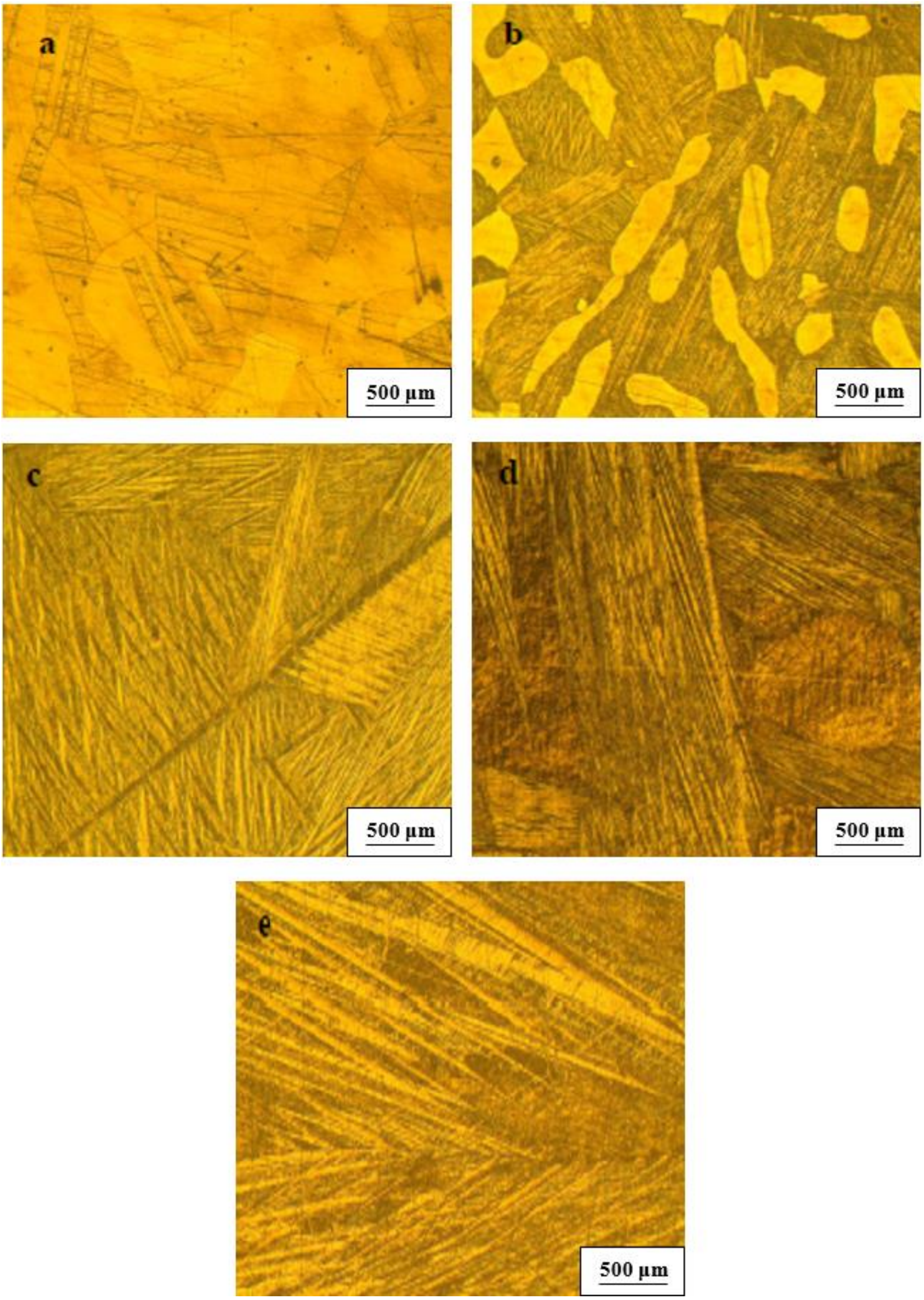

Fig. 3 Optical micrograph of Cu-Zn-Al alloy heated to 850 °C for 10 min and quenched in ice water, **(a)** 0 % Ag, **(b)** 0.12 % Ag, **(c)** 0.15 % Ag, **(d)** 0.25 % Ag, **(e)** 0.35 % Ag.

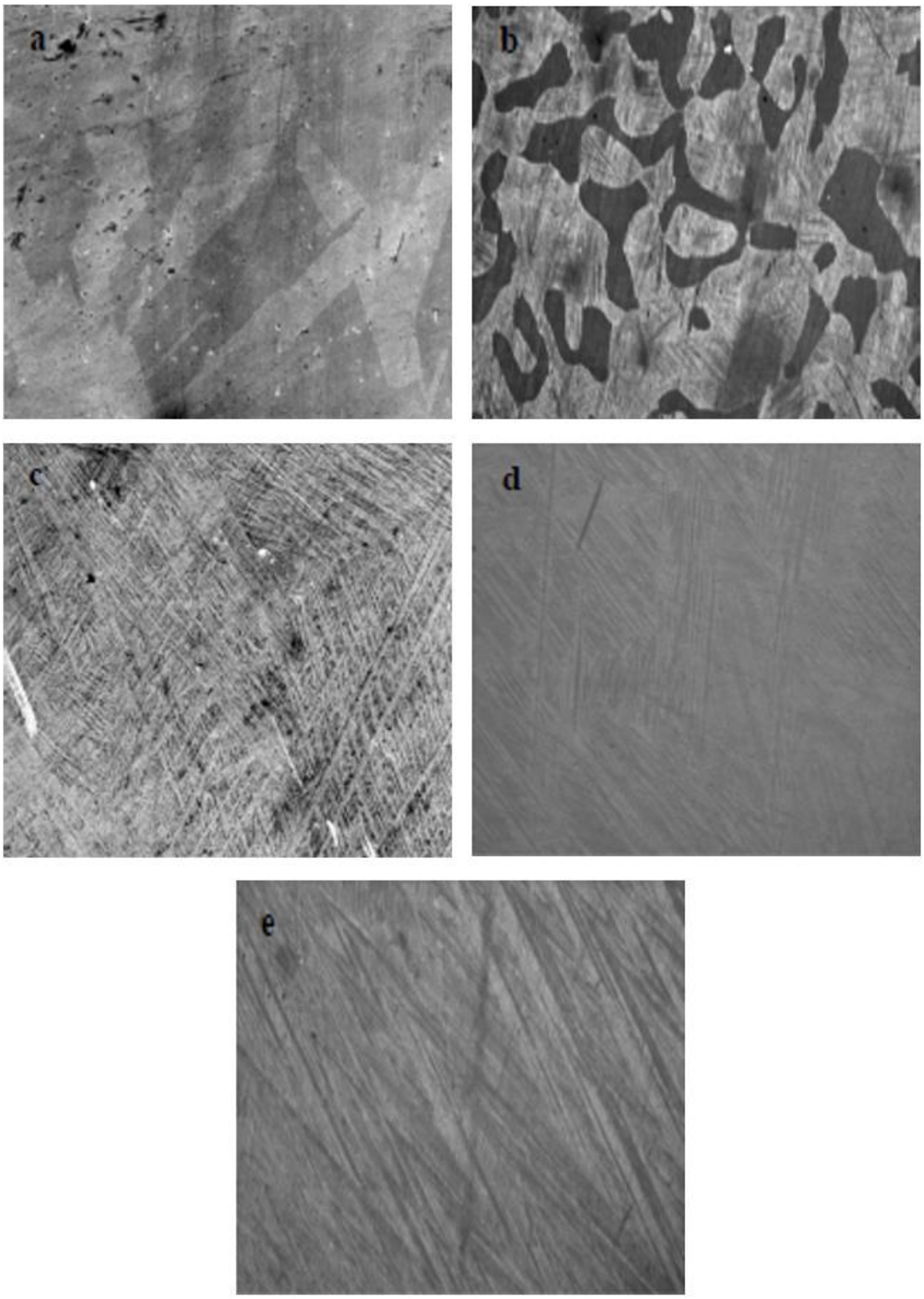

Fig. 4 SEM micrograph of Cu-Zn-Al alloy heated to 850 ℃ for 10 min and quenched in ice water, **(a)** 0 % Ag, **(b)** 0.12 % Ag, **(c)** 0.15 % Ag, **(d)** 0.25 % Ag, **(e)** 0.35 % Ag.

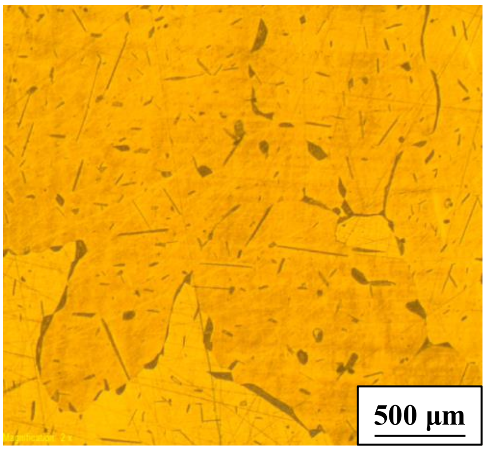

Fig. 5 Optical micrograph of Cu-Zn-Al alloy heated to 900 ℃ for 10 min and quenched in ice water.

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