Fabrication of manganese-aluminum bronze as a shape memory alloy by accumulative roll bonding process

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Abstract

Cu/Al/Mn nanocomposites were produced from copper and aluminum strips and manganese powder using Accumulative Roll Bonding (ARB) and then solid solution treatment was performed to produce shape memory alloy. Two solid solution treatment temperatures (850 and 950°C) were employed to evaluate the phase formation. Scanning electron microscopy, optical microscopy and X-ray diffraction were used for the microstructural and structural studies of the samples. The composition of the produced sample after solid solution treatment at 950°C was also evaluated by energy dispersive X-ray spectroscopy. The results showed that manganese-aluminum bronze, 83Cu-12Al-5Mn (wt.%), was successfully produced by the ARB process followed by heat treatment. The microstructure of the composite annealed at 950°C consisted of a fully martensitic phase after ice-water quenching. In addition, the electrochemical corrosion behavior of the produced nanocomposite and bronze was investigated in a 3.5 wt. % NaCl solution by a potentiostat-galvanostat device. It was found that the corrosion resistance of the bronze alloy is higher than that of the composite due to having a single phase microstructure.

Keywords: Multilayered composite; Shape memory alloy; Heat treatment; Microstructure

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1. Introduction

Shape memory alloys (SMAs) have unique properties which make them a multifunctional material for different applications [1]. Among shape memory alloys, NiTi compounds are widely used in medical and engineering applications, due to their shape memory effect (SME), superelasticity and biocompatibility [2,3]. However, the low transformation temperature and excessive production cost of NiTi alloys reduce their applications, particularly for high-temperature uses [1,4]. Inexpensive Cu-based SMAs have been investigated and developed because of advantages in electrical and thermal conductivities and deformability compared with Ti-Ni-based SMAs [4-7]. The most applicable Cu-based SMAs are in the Cu-Zn and Cu-Al systems. The application of Cu-Al SMAs is limited due to large elastic anisotropy and large grain size [1,8,9]. Therefore, many researches have tried to improve the properties of Cu-based SMAs by the addition of alloying elements (e.g. Ni, Mn, Ti, Be, and so on) [1,5,10-12]. Among the alloying elements, manganese is often added to improve the alloy ductility [10,11]. For instance, it has been reported that Cu-Al-Mn SMAs exhibit more ductility than Cu-Zn-Al and Cu-Al-Ni alloys [5,8,13-15].

The SME in Cu-Al-Mn alloys is based on the thermoelastic martensitic transformation that occurs between a β phase (with DO₃ or L₂, order structures) and a martensitic phase (identified as 3R, 9R, 18R, or 2H structures) [6, 10]. The β phase in the binary Cu-Al alloy system undergoes eutectoid decomposition at about 350 °C into α and γ [16].

However, if it is quenched from the β phase region to ambient temperature, it transforms martensitically [4]. It is known that ordering reactions, $\beta \rightarrow \beta_2$ (CuAl: B₂) $\rightarrow \beta_1$ (Cu₃Al:

DO3) [4,5,16], occur at low temperatures during quenching, according to Cu-Al phase diagram.

Cu-based SMAs are usually produced by melting processes [5,6,10,17,18]. A solid-state method which can be used to produce Cu-based SMAs is accumulative roll bonding (ARB) followed by solid solution treatment. The ARB process which is a severe plastic deformation method consists of roll-bonding of prepared sheets by 50% thickness reduction [19,20]. In this process due to repeating roll-bonding procedure, very high strains are introduced into the materials, and structural refinement is achieved [21,22]. In this process at first, a multilayered composite is produced and then by using a suitable heat treatment it changed to a SMA.

Many researches have been focused on multilayered composites produced by the ARB process [23,24]. But, aluminum bronze alloy fabricated by ARBed multilayered composites and subsequent solid solution treatment is not reported. In the present work, for the first time, ARB accompanied by heat treatment was used to fabricate an aluminum bronze (Cu-12Al-5Mn) as shape memory alloy. Then, the structural characteristics as well as corrosion behavior of the composites were investigated.

2. Experimental procedure

In this research, commercially pure copper and aluminum strips and also manganese powder with the purity levels of 99.9, 99, and 99%, respectively, were used as the primary materials. In order to achieve a nominal composition of 83Cu–12Al–5Mn (wt.%), four Cu and three Al strips with the dimensions of 150×30×0.5 and 150×30×0.3 mm³, respectively, were employed. Prior to stacking the strips, their surfaces were

cleaned by acetone and scratch-brushed with a steel wire brush. Wire brushing removes oxide layers and makes a hard layer on the surface, providing the best condition for bonding [23]. After the surface preparation, three Al strips were placed among four Cu strips, as depicted in Fig. 1, while the Mn powders with an average particle size of 40 micron were dispersed between every two of the layers. This sequence of the stacked layers was used for producing initial sandwiches with a thickness of 2.9 mm and previously-mentioned chemical composition.

The produced sandwich was roll-bonded to about 66% thickness reduction under an unlubricant condition, using a laboratory rolling mill with a loading capacity of 20 tons at room temperature. Then, the length of the sample obtained from this stage was sectioned into two halves. After surface preparation, they were stacked again and rolled to 50% thickness reduction. It was named the one cycle and repeated until 9 cycles, as referred as accumulative roll bonding (ARB).

For the structural investigations of the produced composites after different ARB cycles, XRD measurements were carried out on the rolling direction-normal direction (RD–ND) plane of the ARB processed composites. The XRD experiments were performed by an X-ray diffractometer (XRD, Bruker) using Cu $K\alpha_1$ radiation ($\lambda = 0.15406$ nm). The step size and scan rate was selected 0.03° and 6 sec, respectively. In the present work, the Williamson–Hall formula was used to quantify the XRD data.

The composites produced by 9 ARB cycles were subjected to heat treatment inside a furnace at the environment atmosphere. The heat treatment consisted of solid solution treatment followed by ice water quenching. The composite samples were annealed at two temperatures of 850 and 950 °C for 30 min. The heat-treated composite samples were cut

transverse to the rolling direction and after mounting and polishing, were prepared for structural and microstructural studies. Microstructural and compositional studies were performed on the RD–ND plane by a scanning electron microscope (SEM) (EVO-MA25) equipped with energy dispersive spectroscopy (EDS). SEM images were taken by either backscattered electron or secondary electron modes.

The corrosion performance of the produced composites was carried out by a three-electrode cells assembly. The ARBed samples with an area of 0.5 cm² was exposed as a working electrode. A platinum plate and an Ag/AgCl were used as auxiliary and reference electrode, respectively. The measurements were conducted in a 3.5% NaCl solution at room temperature. Electrochemical polarization measurements were carried out using a potentiostat/galvanostat device (Vertex, Ivium). The corrosion potential and corrosion current density of the produced composites were determined from Tafel curves.

3. Results and discussion

The XRD pattern and Williamson-Hall plot of the Cu/Al/Mn composite produced by the ARB process after three, five and nine cycles are shown in Fig. 2. The Williamson–Hall formula was used to quantify the XRD data, as follows [25,26]:

$$\beta \cos \theta = \frac{K\lambda}{D} + 2\varepsilon \sin \theta \quad (1)$$

where θ is the Bragg angle, β is full width at the half maximum of a diffraction peak, λ is the X-ray wavelength, K is a constant, D is the crystallite size, and ε is the lattice strain. Using this method, the crystallite size of the matrix after three, five and nine cycles was obtained to be about 137, 68.56 and 30.47 nm, respectively. According to the results, the ARB process has successfully developed nanostructured Cu/Al/Mn multilayer

composites. The mechanisms of the nanostructures formation during the ARB process are different in metals. One of the mechanisms in the produced composites is continuous recrystallization. Recent studies suggest that the dominant mechanism of the nano and ultra-fine grains formation in metals with low and medium stacking fault energies (like copper alloys) during the ARB process is continuous and discontinuous recrystallization [27,28]. Another mechanism of the nanostructure formation in the ARBed alloys is grain subdivision [26,28]. This mechanism is dominant in metals with high stacking fault energy like aluminum [26,28,30,31]. The grain subdivision mechanism is stated by the conventional dislocation theory [29]. It has been reported that, according to this theory, in the initial stages of the ARB process dislocations are generated and formed dislocation cells with thick walls. The dislocation cells wall thickness is decreased by increasing the ARB cycles and ultra-fine grains are formed in the ARBed samples [26,28,29].

Since the two different metals from the view point of stacking fault energy are present in the produced composites, both the mentioned mechanisms participate in the structural refinement. The factors that affect the composite structural refinement include [21,24,32,33,34]: a) high straining as a result of repeating ARB cycles, b) friction between the rolls and composite samples under the dry condition and consequently increase of shear strain, c) increasing the dislocations density and therefore structural refinement due to scratch brushing of sample surface, d) increasing the number of layers in composite samples with increasing ARB cycles. During the ARB process the interfaces of these layers inhibit dislocation motion and lead to structural refinement. For instance, in the produced composites, the Al layers are dispersed in the Cu matrix and interface of them act as barriers against dislocations motion. In addition, new dislocations

may generate around these layers and help to structural refinement. e) the role of the Mn particles in prevention from grain growth during the ARB process. In addition, it should be noted that after nine ARB cycles, a uniform distribution of the Mn particles in the matrix is obtained. The Mn particles similar to the Cu/Al interface can be considered as barriers to dislocation motion and leads to structural refinement, f) the difference in the coefficients of the thermal expansion of the Cu, Al, and Mn can affect the dislocation generation during the ARB process and consequently structural refinement [33]. Due to friction between the rolls and composite samples, the constituents' temperature increases during the ARB process. When the composite samples are starting to cool down after the ARB process, thermal stresses at the interface of the constituents are produced due to their different thermal expansion coefficients. These thermal stresses lead to the production of new dislocations and therefore structural refinement. Note that the thermal expansion coefficients of Cu, Al and Mn are 17, 23.6 and 21.7 $\mu\text{m/mK}$, respectively.

Fig. 3 depicts the EDS elemental mapping and point spectrum of the Cu/Al/Mn composite produced after nine ARB cycles. As it can be seen, the Al and Mn constituents have been homogeneously distributed in the Cu matrix. Although an atom-to-atom bonding between the sample constituents is created during the ARB process [35], a specific alloy is not formed in the produced composite. Accordingly, an appropriate heat treatment can be used for creating the alloy from the produced composite. In this study, the nanostructured composites produced by nine ARB cycles were heat treated in order to produce an aluminum bronze alloy with 83Cu-12Al-5Mn (wt.%) composition. For this purpose, the ARBed samples were annealed at 850 and 950°C, i.e. at the β phase formation temperature range, and then ice-water quenched.

Fig. 4 shows the SEM image of the sample heat-treated at 850°C for 30 min after quenching in the ice-water bath at two different magnifications. As can be seen from the images, the microstructure consists of two main region, a bright matrix and dark islands inside the bright matrix. The needle-like shape of the matrix confirms the presence of martensite, while the dark regions should be secondary phases. From the binary phase diagram of Cu-Al [16], it can be seen that by heating the produced composite samples to 850°C, the present phase in the sample should be the β phase, where after ice-water quenching it is transformed to the β' phase. However, according to Fig. 4 after cooling the sample, the microstructure consists of more than two distinct phases. It should be noted that, the presence of secondary phases (in addition to martensite) in the microstructure is attributed to structural non-homogeneity due to inappropriate heat treatment conditions. Indeed, at this treatment (i.e. 850 °C for 30 min), diffusion between the present elements was not completed to reach a structural homogenization. In fact, because of heat treatment at a low temperature (like 850 °C), diffusion between the initial constituents (Cu, Al, and Mn) was not sufficient for the complete formation of the β phase; therefore, the martensite phase and dark regions were obtained after quenching.

By increasing the heating temperature to 950 °C, the microstructure has changed, as shown in Fig. 5. As can be seen in this figure, a single-phase structure consisting of very thin martensitic plates, as shown by arrows, is obtained. Fig. 6 shows the OM image of the specimen heat-treated at 950 °C after quenching in the ice-water bath. As it can be seen, the martensite phase with a fine needle-like structure is clearly visible in the figure. This needle-like structure is similar to that of Cu-Al-Mn shape memory alloys produced by melting methods [36,37].

Fig. 7 shows the composition distribution of Cu, Al, and Mn elements in the produced alloy after solid solution treatment at 950 °C using the EDS technique. As can be seen in the figure, this alloy has a homogeneous microstructure in which some small pores are seen. The presence of these pores is attributed to the Kirkendall effect accompanied by a volume shrinkage associated with the compound formation [23].

In order to recognize the phases shown in Fig. 4, the XRD analysis was performed on the sample heat-treated at 850 °C, as shown in Fig. 8. As it is observed, the presence of the martensite phase as the β' phase is conformed. Moreover, from the XRD pattern, it was found that the secondary phases are Cu_3Al and Cu solid solution. From the binary phase diagram of Cu-Al [16], it can be seen that with Al concentrations more than 11 wt.%, the disordered β lattice is transformed into the ordered β_1 structure (DO_3 or Fe_3Al type structure) at the order-disorder transition temperature.

By comparing the XRD pattern of the samples heat-treated at 850 and 950 °C (Fig. 8), it is revealed that 950 °C is an adequate temperature for the heat treatment of the produced composite. In this temperature, diffusion between the initial constituents (Cu, Al, and Mn) is completely performed and a homogeneous β phase is created. Consequently, after quenching, the β' martensite phase is created from the β phase with no secondary phases. The XRD analysis of the samples heat-treated at 950 °C confirms the SEM results and proves that all the peaks belong to the martensite phase (β').

Since SME is based on crystallographic reversible thermoelastic martensitic transformations, the presence of the martensite phase at Cu/Al based alloys is crucial for this effect [5,6,10,11,15]. Moreover, in the produced Cu-Al-Mn alloy, it is proved that the martensite phase as well as the parent phase can be produced at different conditions. In

this regard, it can be concluded that in the present composite system, the martensitic transformation temperatures are above room temperature. In addition, the potential to produce the parent and martensite phases indicates that the produced composite is susceptible to show SME.

Potentiodynamic polarization tests in a 3.5% NaCl solution were performed to evaluate the corrosion behavior of the produced Cu/Al/Mn composite before and after heat treatment at 950 °C followed by quenching in ice water. The polarization curves of the samples and the extracted data are shown in Fig. 9 and Table 1, respectively.

According to the curves shown in Fig. 9, for both the samples, the cathodic branch of the polarization curves represents the hydrogen evolution, while the anodic branch shows the alloy dissolution. There are three regions in the anodic branch of the polarization curve: the apparent Tafel region, the passive region (where there is a tendency of the electrode to passivation) and the transpassive region (in which the current density rises again with the positive potential changes). This anodic behavior is a typical anodic behavior for dissolution of copper and copper alloys in chloride solutions [38, 39].

As can be seen from the curves, the corrosion potential of the produced alloy calculated by the Tafel extrapolation is more positive than that of the produced composite. This shift means that the corrosion reaction of the Cu-Al-Mn alloy is suppressed by the β' single phase formation. Moreover, the corrosion current density (i_{corr}) of the produced alloy, which is the relative measure of the corrosion rate, is less than that of the produced composite. So that, using heat treatment, the corrosion current density is decreased from $6.5 \mu\text{A}/\text{cm}^2$ to $1.78 \mu\text{A}/\text{cm}^2$ (Table 1). The corrosion current density, i_{corr} ($\mu\text{A}/\text{cm}^2$), is related to the corrosion rate, P_i , through the following empirical equation [40]:

$$P_i = 22.85 i_{\text{corr}} \quad (2)$$

According to the equation, the corrosion rate of the Cu-Al-Mn alloy is decreased from 148.52 $\mu\text{m}/\text{year}$ to 40.67 $\mu\text{m}/\text{year}$ for the composite and heat-treated alloy, respectively. The reason for this behavior is attributed to the formation of corrosion products on the alloyed sample surfaces, which act as barrier films to protect the surfaces from aggressive solutions [1, 12, 38]. According to the literature, this decrease in the current density is due to the formation of some oxide compounds on the surface. It has been reported that in Cu/Al alloys, copper and aluminum dissolution occurs, which results in the formation of cuprous oxide (Cu_2O) and aluminum oxide/hydroxide ($\text{Al}_2\text{O}_3/\text{Al}(\text{OH})_3$) [1,12, 38, 41]. In addition, it is possible that manganese oxide is produced on the surface due to the presence of Mn element in the alloy [41].

By the formation of these corrosion products (the protective oxide films) on the alloy surface, the anodic reaction will be controlled by the inhibition of the diffusion rate of OH^- , Cl^- , and Cu^+ [41]. It should be noted that the higher corrosion rate of the composite sample is attributed to the formation of galvanic couples due to the potential differences between Cu, Al, and Mn elements in the 3.5% NaCl solution. In addition, the presence of a high dislocation density as a result of the ARB process accelerates the tendency to the loss of electrons and release of ions into the electrolyte [42].

Based on Fig. 9 and Table 1, the passivation of the produced alloy takes place at a higher current density and passivation potential, in comparison to the non-heat treated composite. After the passivation region, the polarization curves of the two samples possess a breakdown at higher anodic potentials (at around -0.8 and 1.8 V vs Ag/AgCl for the samples before and after heat treatment, respectively). A low E_{bd} as well as a short

passive range in the non-heat treated composite confirm that corrosion products are not sufficiently adhesive and their stability is comparatively poor. Pitting, which occurs at potentials higher than E_{bd} in the alloy, is accompanied by the removal of Mn/Al-rich surface oxides and the accumulation of products around the pits. These losses can be qualitatively explained by localized galvanic reactions in the alloy [5, 41]. The surface morphology of the produced composite after the corrosion test is shown in Fig. 10, in which some pits were detected in the matrix.

The comparison of corrosion behavior between the produced alloy and Cu-Al-Ni-Mn shape memory alloy produced by the casting method shows that their corrosion potential and current density is the same [41]. For instance, the corrosion potential and current density of the Cu-Al-Ni-Mn shape memory alloy produced by the casting method are - 0.277 V and $1.58 \mu\text{A}/\text{cm}^2$ [41], respectively, which are approximately close to those of the produced alloy (see Table 1).

4. Conclusions

Accumulative roll bonding followed by solid solution treatment was applied to produce manganese aluminum bronze with the composition of 83Cu-12Al-5Mn (wt.%). The outcome of this study can be summarized as follows:

1. A nanostructured Cu/Al/Mn composite with the average matrix crystallite size of 30.47 nm was successfully fabricated by the ARB process at room temperature after 9 cycles.
2. No new phase was found in the as-rolled composites even after 9 cycles.
3. The solid solution temperature had a significant effect on the microstructure and phase formation.

4. With increasing the temperature of heat treatment from 850 °C to 950 °C, multiphase (Cu_3Al , α , and β') structure changed to β' single phase structure.
5. Accumulative roll bonding followed by the solid solution treatment was a feasible process to produce Cu-Al-Mn alloy.
6. Quenching of the produced composites from the β phase formation temperature in a ice water bath resulted in the formation of needle-like structure (martensite).
7. The corrosion current density of the produced samples is decreased from $6.5 \mu\text{A}/\text{cm}^2$ to $1.78 \mu\text{A}/\text{cm}^2$ by heat treatment.

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Figure captions:

Fig. 1. Schematic of the strip stacking sequence for the 7-layers specimens subjected to ARB.

Fig. 2. XRD pattern (a) and Williamson-Hall plot (b) of the composites processed by 3, 5 and 9 ARB cycles.

Fig.3: (a) SEM image of Cu/Al/Mn composite after 9 cycles and the corresponding SEM elemental maps for (b) Cu distribution, (c) Al distribution, and (d) Mn distribution. (e) Point spectrum of the Cu/Al/Mn composite.

Fig. 4. SEM backscattered electron images of the sample heat-treated at 850 °C.

Fig. 5. SEM images of the sample heat-treated at 950 °C.

Fig. 6. OM images of the composite samples after heat treating at 950 °C.

Fig. 7. (a) SEM image of the sample heat-treated at 950 °C. Related EDS elemental maps showing, (b) Cu, (c) Al, and (d) Mn distributions. (e) Point spectrum of the sample heat-treated at 950 °C.

Fig. 8. XRD patterns of the samples heat-treated at 850 and 950 °C.

Fig. 9. Potentiodynamic polarization curves of the produced Cu-Al-Mn composites before and after heat treatment in the 3.5 wt. % NaCl solution.

Fig. 10. SEM micrograph of the produced Cu-Al-Mn composite after the corrosion test in the 3.5% NaCl solutions.

Table

Table 1

Parameters derived from the potentiodynamic polarization curves for the produced nano-composite and alloy.

Sample	E_{corr} (V)	i_{corr} ($\mu\text{A}/\text{cm}^2$)	E_{pp} (V)	E_{bd} (V)	$E_{\text{bd}}-E_{\text{pp}}$ (V)	Pi ($\mu\text{m}/\text{year}$)
Composite	-1.25	6.50	-1.05	-0.80	0.25	148.52
Alloy	-0.25	1.78	0.20	1.80	1.60	40.67

Fig. 1

Fig. 2

Fig. 3

Fig. 4

Fig. 5

Fig. 6

Fig. 7

Fig. 8

Fig. 9

Fig. 10