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Study of effect of Fe, Cr and Ti on the martensite phase formation in Cu-12.5 wt% Al-5wt % Mn SMA

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Abstract

Copper based shape memory alloys are studied throughout the world for their high transition temperatures and high thermal stability. Among Copper based shape memory alloys(SMAs), Cu-Al-Mn SMAs have shown good ductility and high transition temperature. Only those alloy systems that can show the formation of β phase are capable to demonstrate the shape memory properties. In this paper the effects of the alloying elements on the formation of martensite phase have been studied exclusively. Addition of 1 wt% of Fe, Cr and Ti to the Cu-12.5Al-5Mn shape memory alloy has been investigated in detail. Therefore, four alloys have been synthesized through liquid metallurgy route using pure metals of 99.9% purity in a melting furnace weighing 1kg each. Samples were heat treated at the temperature of 920˚C for 2 hours and then quenched in ice water. The optical micrographs show the formation of the martensite structures in all the samples except in the samples in which 1 wt% Fe was added. X-Ray diffractions also revealed the same facts as obtained in the optical microscopy. Vickers Hardness of all four samples were carried out. The result shows no sign of martensite formation in sample containing Fe; therefore, this alloy should not be used for further study in the direction of understanding shape memory behaviors of the copper based shape memory alloys. Moreover, it was also observed that the addition of Cr yielded good martensitic formation as compared to the alloy containing Ti. Copyright © 2016 VBRI Press.

Keywords: Cu-Al-Mn , shape memory alloy, martensite, X-Ray diffraction, alloying addition.

Introduction

Shape Memory Alloys (SMAs) are smart materials which have unique properties of remembering their shapes and ability to recover their original shape even after plastic deformation on the subjection of heat or magnetic field. These are materials of recent interests in the field of automotive, biomedical, robotics, costumes, aerospace sectors, etc. The growing demand of automation in virtually every technological sectors have increased the use of sensors, actuators, artificial intelligence systems which consequently have unnecessarily increased the weight, cost and volume of the smart systems. Therefore, shape memory alloys can prove the revolutionizing solution for these problems.

Presently, SMAs can be classified into three alloy systems: NiTi alloys, Copper based SMAs and Iron based alloys. Furthermore, Copper based SMAs can be divided into three major alloy systems, that is, Cu-Al-Ni alloys, Cu-Al-Mn alloys and Cu-Zn-Al alloys. Copper based shape memory alloys are one of the most studied alloy system among the researchers other than Nitinol. These copper based shape memory alloys have a strong potential to become the alternative to the commercially available NiTi SMA system. NiTi alloys are expensive, hard to process and possess low transition temperatures. Unlike them, copper based shape memory alloys are easy to synthesize, cheap and have high transition temperatures. This makes these alloys applicable to the industry working at high temperature. There is a huge demand for higher operating temperatures for actuators in the industries which can solved by making high transition temperature of shape memory alloys **[1]**.

Among copper based SMAs, Cu-Al-Mn alloys show high ductility **[2]** and good shape memory characteristics **[3]**. But these alloys have certain limitations such as majority of the compositions show brittleness and poor workability. They show low bandwidth and poor fatigue life which limit their commercial applications. In order to solve these limitations several approaches have been used such as alloying addition, variation in the composition of the constituents in an alloy system which reduces the grain sizes **[4]**, adopting different heat treatment cycles **[5]**, secondary deformations technique etc.

Alloy synthesized through powder metallurgy route produces smaller grain size than that of liquid metallurgy route but the issue 100% density is involved in former technique **[6]**. Shape memory properties of SMAs are highly sensitive to their chemical compositions.

Cu-Al binary alloy system possesses cubic centered β phase which shows martensitic transformation. Addition of ternary and quaternary elements to Cu-Al results in adjusting the transition temperature of these alloys **[7]**. In this paper, the effects of addition of elements Fe, Cr and Ti to the Cu-12.5Al-5Mn alloys have been investigated in terms of microstructural changes, X-Ray diffractions and Vickers hardness. It has been reported by Ashish et. al. that Al:Mn ratio of 0.8 and 3 show superior shape memory properties **[8]**. Therefore, the composition of alloys of present study has been selected accordingly. Though these element alloying additions have been studied earlier but with different combination of heat treatment cycles and composition of the alloys, than that of the present work. Therefore, this work carries out the new investigation in the study of microstructural changes in the Cu-12.5Al-5Mn due to above stated reason, and which ensures the further investigation of potential alloys.

Experimental

Materials

Four alloys (namely A, B, C and D) of Cu-Al-Mn based system were prepared through liquid metallurgy routes. The melting furnace was used for melting the alloy under inert atmosphere of argon gas. Melting of the alloys were carried out at CSIR-AMPRI, India. Pure metals (Kowa Abrasives, Japan) of copper, aluminum, manganese, iron, chromium and titanium of 99.99%purity each were used to synthesize the alloys. 1 Kg of each composition was melted and then was casted in a graphite die in form of fingers.

Materials characterization

Alloys synthesized after casting were cut in proper shapes and sizes in order to prepare samples for further characterizations. The samples were heat treated at temperature of 920°C for 2 hours in a muffle furnace; and thereafter were quenched in ice water. The samples were cut into required shapes and sizes using grinder and were polished using standard metallography techniques with the aid of automatic polishing machine (Buehler, EcoMet 3000, USA). The polished samples were etched in a solution of 25 mL HCl+5mL $FeCl_3$+100 mL C_2H_5OH.The properly etched polished samples were observed under the optical microscope (LEICA, Metalloplan, Germany) for the microstructural developments of different phases. The XRD of the quenched samples were carried out in an X-Ray Diffractometer (Bruker, D8 Advanced, Germany) at room temperature. The 2θ variation was from 10° to 90° at the speed of 0.01°/s using Cu Kα target. The Vickers hardness of the samples was taken using universal hardness tester (KB 250 BVRZ, Pruftechnik, Germany) with a load of 5kgf. Three indentations were made on each sample, and were averaged to calculate the hardness of the alloys.

Results and discussion

Chemical analysis

The chemical analysis of the cast samples was carried out for each targeted alloy using Optical Emission Spectrometer (Bruker, Q4 TASMAN, Germany). The result obtained after chemical analysis are summarized in the **Table 1** shown below. The percentage of Fe in the sample B was found close to the target but Ti and Cr were found in small traces.

Table 1. Actual compositions of alloys synthesized.

S. No.	Composition & Sample Description	Sample Name	Chemical Analysis					
			Cu	Al	Mn	Fe	Cr	Ti
1	Cu-12.5Al-5Mn	A	83.0	12.27	4.64	--	--	--
2	Cu-12.5Al-5Mn-1Fe	B	83.60	12.61	2.39	1.07	--	--
3	Cu-12.5Al-5Mn-1Cr	C	84.19	12.77	2.66	--	0.03	--
4	Cu-12.5Al-5Mn-1Ti	D	83.67	11.90	3.70	--	--	0.37

The obtained chemical compositions after casting differ from that of targeted. The percentage of alloying elements and base alloys differ significantly.

Microstructure

The optical micrographs of the samples are shown in the **Fig. 1**. The **Fig. 1** shows the microstructures of the cast and quenched samples of each composition namely A, B, C and D. Sample A shows good formation of martensitic structure after quenching **(Fig. 1(b))**. Cast alloy of sample A **(Fig. 1(a))** shows a regular formation of α+β phases which is prerequisite microstructural feature for alloy to form martensitic phase upon quenching. This indicates the potential of the alloy to exhibit shape memory properties **[9]**.

Cast alloys of samples B, C and D show two phase structures with increased precipitations as compared to that of cast alloy of sample A; which show scanty precipitation. It can also be observed from the micrographs of the cast alloys of the samples B, C and D that addition of quaternary alloying elements to the base alloy (Sample A) have resulted in reduction of grain size comparatively **(Fig. 1(c, e, g))**. This is a favorable result in case of present study since large grains are one of the major problems associated with these copper based shape memory alloys. Precipitation of the second phases may have occurred due to their limited solubility in the parent matrix at the room temperature. These precipitations of second phase are also confirmed in the X-Ray diffraction plots in **Fig. 2**. The precipitations have occurred throughout the grain matrix and along the grain boundaries. However, the precipitation of second phase is less in cast alloy of Sample D **(Fig. 1(g))** as compare to that of sample B and C. This may be happened owing to the fact that some titanium was consumed in forming base matrix.

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Quenched alloys of Samples A, C and D have shown good formation of martensitic structures as shown in **Fig. 1(b, f, h)**. Both types of martensite, that is, $\beta_1^{'}$(18R) and $\gamma_1^{'}$(2H) are obtained in these quenched alloys in varying proportions **[10]**. Both these martensite phases are ductile in nature and show good shape memory properties. Therefore, these alloys have the potential for showing shape memory properties. Martensite plates show regular and parallel orientations in quenched alloys of samples A and D whereas in sample C, they are zig zag and branched.

However, the quenched alloy of sample B show no traces of martensitic structures **(Fig. 1(d))**; although addition of 2 wt% of iron to Cu-12.5Al-5Al alloys showed the formation of martensite phase as reported by Shahadat et al. **[11]**. For the same alloy system with different compositions, Canbay et. al. reported the presence of 18R martensites in their samples **[12].**

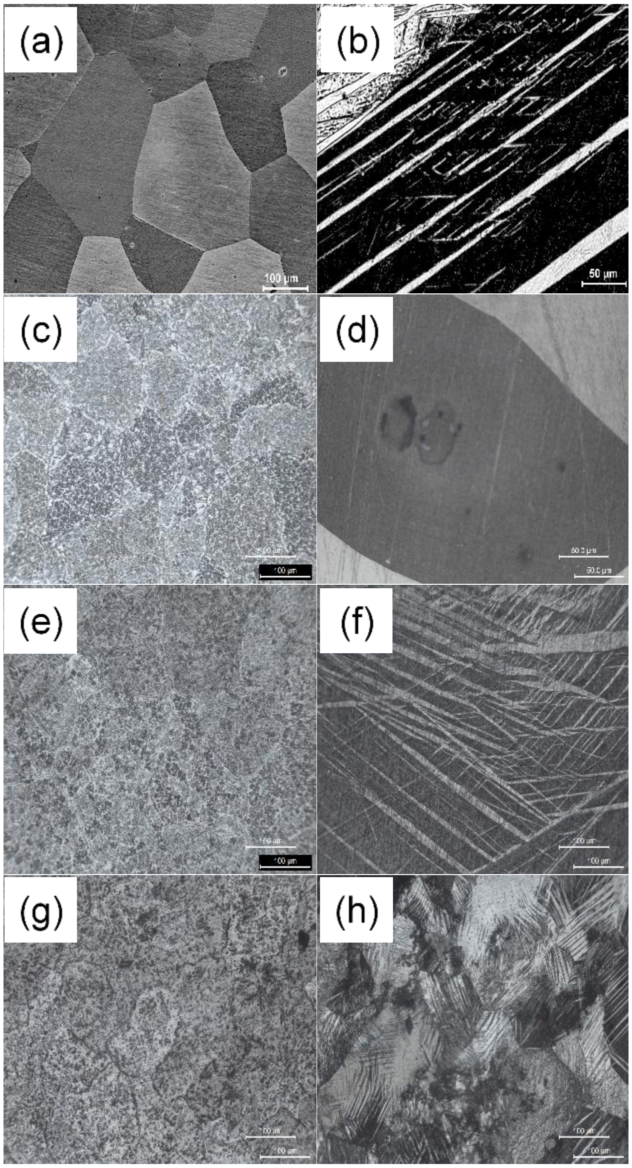

Fig. 1. Optical micrographs of the Sample A, Sample B, Sample C, Sample D cast (a, c, e, g, respectively) and quenched samples (b, d, f, h, respectively).

X-Ray diffraction (XRD) analysis

The presence of martensite phase may indicate the completion of martensitic phases in these samples. However, no such martensitic phases are observed for sample B in the XRD plots as well as in optical micrograph. The martensitic phases of Al_2Cu_3 ($\beta_1^{'}$) and Al_4Cu_9 ($\gamma_1^{'}$) have been clearly identified in samples A, C and D respectively.

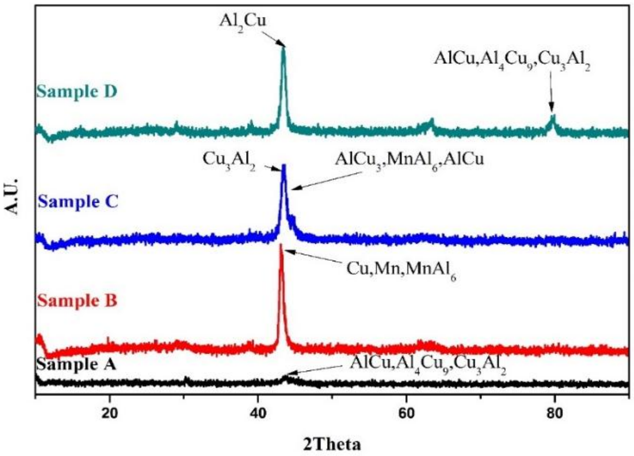

Fig. 2. XRD plots of the quenched.

Mainly the phases related to Cu and Al were identified in the X-Ray diffraction studies owing to the fact that are in major proportions in composition in all the samples as compared with that of other elements. However, no martensite phases were identified in the quenched alloy of Sample B unlike as reported by Canbay et al. for different compositions of present alloy system in which 18R martensites were found in X-Ray diffraction analysis **[12]**.

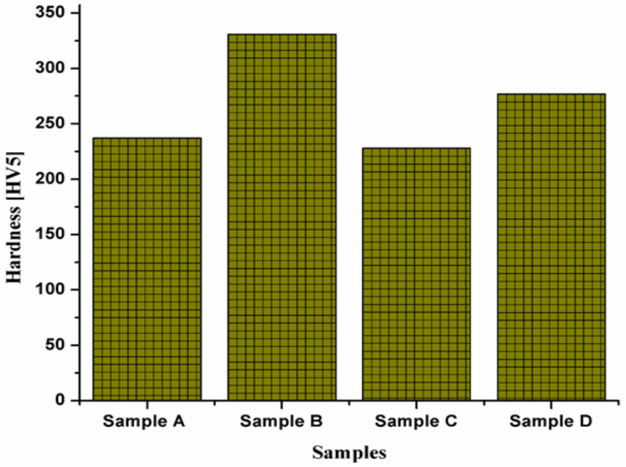

Fig. 3. Hardness of the quenched samples.

Hardness

The hardness of the samples was taken using Vickers hardness tester with the load of 5 kgf. The values of hardness of quenched samples are shown in **Fig. 3**. It can be clearly seen that the hardness of Samples B, C and D are greater than that of Sample A. Moreover, it can be observed from the bar chart that the hardness of sample B is higher as compared with other samples. It is generally known that the martensitic phase in non-ferrous alloy is softer as compared with other phase. Since samples A, C and D show good formation of martensite phase as compared with sample B which show no sign of martensite formation, the hardness of sample B is consequently higher than that of others.

Conclusion

Grain structure with α+β phases can be seen in all four samples in cast condition which indicate their potential for demonstrations of shape memory behaviors since The addition of chromium and titanium have resulted into good martensite formation in the Samples C and D respectively upon quenching in ice water. However, the addition of iron to the base alloy Cu-12.5Al-5Mn alloy (Sample A) resulted into formation of no martensite phase in the sample B upon quenching. The above facts observed in the optical micrographs were also observed in XRD analysis of the all four quenched samples. The martensite phases Al_4Cu_9(γ'), Al_2Cu_3 and $AlCu_3$ were found in Samples A, C and D but no such phases were found in sample B. The hardness of the sample B was found to be higher than that of the other three samples indicating the probable absence of martensite phase in sample B owing to the fact that hardness of martensite phase is lower than austenite phase in case of non-ferrous alloys as compare to that of ferrous alloys.

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Author's contributions

Conceived the plan: Shahadat, Rupa Dasgupta; Performed the expeirments: Shahadat, Ashish,Ayub; Data analysis: Shahadat, Abhishek, Rupa Dasgupta; Wrote the paper: Shahadat, Rupa Dasgupta. Authors have no competing financial interests.

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