Transactions of The Indian Institute of Metals

Vol. 64, Issues 1 & 2, February-April 2011, pp. 165-168

Influence of aluminium and iron contents on the transformation temperatures of Cu-Al-Fe shape memory alloys

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Received 01 November 2010 Revised 17 February 2011 Accepted 23 February 2011 Online at www.springerlink.com © 2011 TIIM, India

Keywords:

shape memory alloys; transformation temperatures; shape memory effect.

Abstract

Copper based shape memory alloys have received much focus in recent times because of their good ductility, ease of production and processing and low cost. Earlier investigations have shown that ductility and other mechanical properties of the Cu-Al based shape memory alloys can significantly be improved by adding ternary elements such as Ni and Mn. While Cu-Al-Ni shape memory alloys have better thermal stability and higher operating temperatures, their practical applications are limited because of their poor workability. Cu-Al-Mn shape memory alloys on the other hand, have good ductility and workability, but their operating temperatures are lower. A similar approach is followed in Ni-Al alloys to overcome their brittleness by the addition of Fe. There is paucity of literature on the role of ternary addition of Fe to Cu-Al shape memory alloys. In the present work, therefore, the effect of aluminium and iron on the transformation temperatures has been studied. As the aluminium content increases the transformation temperatures decrease, while the ternary addition of Fe increases the transformation temperatures. The results are presented and discussed in detail in the paper.

1. Introduction

Shape memory alloys have been studied as well as used extensively over the years capitalizing on their two unique properties, namely shape memory effect (SME) and superelasticity (SE). These two unique properties are attributed to the solid state transformation of martensite to austenite and vice versa. For many years shape memory alloys (SMAs), such as those based on NiTi, Cu and Fe have been found to be attractive for commercial applications. Cu-based SMAs are attractive for the manufacture of gadgets/devices based on SME and SE because of their low cost coupled with good shape memory effect. Cu-Zn-Al, Cu-Al-Ni and Cu-Al-Mn are some of the Cu-based SMAs which are popular due to their wide range of transformation temperatures. Among the aforesaid Cu-based alloys only Cu-Al-Ni SMAs can be used at temperatures near 200°C [1,2].

Recently researchers are showing increasing interest in SMAs that can function at high temperatures (over 200°C) in aerospace and automobile industries. As a result, several SMAs with high transformation temperatures have been developed. Some of the alloys that are of worthy of mention here are: NiTiZr, NiTiHf, NiTiPd, NiAl and NiMnGa SMAs. But among these SMAs NiTiZr and NiAl have the drawback of high brittleness, while high temperature SMAs, such as NiTiPd, are of high cost. Due to these reasons there is a constant search for new and low cost shape memory alloys that can perform satisfactorily at high temperatures [3].

Shape memory alloy based on binary Cu-Al with Fe as a ternary addition have been studied by the present authors. The addition of Fe has modified the nature of the martensitic transformation, revealing a thermoelastic transformation and SME. Like various other Cu-based SMAs, Cu-Al-Fe alloys exhibit martensitic transformation when the disordered β phase, which is usually stable at high temperatures, is quenched from the β field region to undergo an ordering reaction $\beta \rightarrow \beta_2 \rightarrow \beta_1$ and subsequently to ordered martensites: α' , β' , γ' depending on the composition of the alloys.

In the present study, Cu-Al-Fe alloys with different compositions were studied for their microstructures and transformation temperatures. The results are promising, and go to prove that the alloys can satisfactorily function at high temperatures.

2. Materials and Methods

Two sets of Cu-Al-Fe alloys, one with almost a constant Cu/Fe ratio and varying Al contents, and the other with almost a constant Cu/Al ratio and varying Fe contents, were selected for the investigation. These alloys were obtained by melting the pure metals in an induction furnace under an inert atmosphere of argon. One set of alloys was labeled S1, S2, S3, S4 and S5, and the other set S6, S7 and S8. The specimens obtained from these alloys were homogenized at 900°C for 1h under an argon atmosphere. The alloy samples were then hot rolled at 800°C to a thickness of 1mm. The rolled samples were betatized for 30 min at 900°C and step quenched into boiling water (100°C) and then quenched into a water bath at room temperature.

Optical microscopy was used to study the microstructure and morphology of the martensites formed. Differential scanning calorimeter at a heating and cooling rate of 20°C/min. The phases present in the samples were determined by X-ray diffraction using Cu-K_{α} radiation. The chemical compositions were determined by atomic absorption spectrometry by removing samples from different parts of the alloys cast.

3. Results and discussion

The chemical compositions and transformation temperatures of the alloys having almost a constant Cu/Fe ratio and varying Al contents are tabulated in Table 1 and that for the alloys having almost a constant Cu/Al ratio with varying Fe contents are tabulated in Table 2.

Table 1 : Chemical compositions and transformation temperatures of the alloys having almost a constant Cu/Fe ratio and varying Al contents

Alloy ID	Chemical Composition			Transformation Temperatures (°C)			
	Си	Al	Fe	M_{f}	M_s	A_s	A_f
S1	85.19	10.21	4.60	243	308	416	478
S2	84.51	11.17	4.42	232	255	395	450
S3	83.86	11.56	4.58	203	232	311	371
S4	83.76	11.91	4.62	171	203	200	227
S5	83.05	12.60	4.35	114	135	131	160

Table 2 : Chemical compositions and transformationtemperatures of the alloys having almost a constantCu/Al ratio and varying Fe contents

Alloy ID	Chemical			Transformation			
	Composition			Temperatures (^{o}C)			
	Си	Al	Fe	M_{f}	M_s	A_s	A_f
S6	86.10	12.55	1.32	240	250	288	372
S7	85.29	12.60	2.11	192	259	399	447
S8	84.83	12.57	2.60	181	266	410	445

Figure 1 shows the DSC curves for alloys with a constant Cu/Fe ratio and varying Al contents. The transformation on heating from martensite to austenite (forward transformation) is endothermic and that on cooling from austenite to martensite is exothermic. It is observed that as the aluminium content increases the transformation temperatures decrease. It shows the dependence of transformation temperatures on chemical composition. The DSC curves for alloys S1 [Fig. 1(a)] and S2 [Fig.1 (b)] show a single sharp peak in both forward and reverse transformations indicating a smooth transformation. In the alloys S3 [Fig.1(c)] and S4 [Fig.1 (d)] the transformation is characterized by two separate peaks, especially in the reverse transformation, indicating the occurrence of $\beta_1 \rightarrow \gamma' + \beta'$ transformation [Fig.1(c) and (d)]. The forward transformation peak on the high temperature side is due to $\gamma_1' \to \beta_1$ transformation and the transformation on the low temperature side is due to $\beta_1 \rightarrow \beta_1$ transformation. In the reverse transformation there are two separated peaks due to the different martensites and their hysteresis. The small peak on the high temperature side is due to $\beta_1 \rightarrow \gamma_1'$ transformation. The sharp peak on lower temperature side is due to $\beta_1 \rightarrow \beta_1'$ transformation. Figure 2 shows the DSC curves for the alloys with almost a constant Cu/Al ratio and varying Fe contents. The alloys S6 and S7 [Fig.2 (a) and (b)] show a sharp peak in both forward and reverse transformations, indicating complete transformation of austenite to martensite. The alloy S8 [Fig.2(c)] shows a broadened peak in forward transformation and twin peaks in



Fig. 1 : DSC curves for alloys with a constant Cu/Fe ratio and varying Al contents



Fig. 2 : DSC curves for alloys with a constant Cu/Al ratio and varying Fe contents

the reverse transformation. The twin peaks give an indication of transformation from $\beta_1 \rightarrow \gamma_1'$ on high temperature side, but a split in the peak in forward transformation is not observed because of the broadening of the peak. It also shows, that as the iron content increases there is an increase in the M_s and A_s temperatures, though to a lesser extent [4-6].



Fig. 3 : X-ray diffraction patterns for the alloys with almost a constant Cu/Fe ratio and varying aluminium contents.



Fig. 4 : X-ray diffraction patterns for the alloys with a constant Cu/Al ratio and varying iron contents.

It is observed from Fig.3(a) and Fig.3(b), that in the alloys S1 and S2 the major phase formed after homogenization and step quenching is β_1 ' martensite. But in the alloys S3 [Fig. 3(c)] and S4 [Fig. 3(d)] it is observed that both β_1 ' and γ_1 ' martensites are present. The amount of β_1 ' martensite present is large in the case of alloy S3 and that present in the case of alloy S4 has an almost equal amount of both β_1 ' and γ_1 ' martensites. The alloy S5 [Fig.3 (e)] has γ_1 ' as the major phase. The proportion of martensites formed in the alloys influences the shape memory effect. It is observed from the X-ray diffraction patterns that at lower aluminium contents the major phase formed is β_1 ' and γ_1 ' martensites are present with γ_1 ' martensite as the major phase.

Comparing the X-ray diffraction patterns of the alloys S6 [Fig. 4(a)], S7 [Fig.4 (b)] and S8 [Fig.4(c)], it is observed that at lower iron contents the amount of β_1 martensite formed



Fig. 5 : Optical micrographs of the alloys with a constant Cu/ Fe ratio and varying Al contents



Fig. 6 : Optical micrographs of the alloys with a constant Cu/ Al ratio and varying Fe contents

is high and at higher iron contents the amount of γ_1 ' martensite formed is high. But in all the alloys both types of martensite can be observed [7-10].

The optical micrographs of the alloys S1 and S2 [Fig. 5(a) and Fig. 5(b)] show predominantly β_1 ' type thin martensitic plates and with a self-accommodating nature, which is characteristic feature of β_1 ' type martensite. Nucleation of martensitic plate groups at numerous sites within the grains can also be seen. The optical micrograph of the alloy S3 [Fig.5(c)] shows a plate like morphology, but the martensitic plates are coarser. This is due to the change in the

composition of the alloy, i.e., increase in the aluminium content. It also shows a mixture of β_1 ' and γ_1 ' martensites, and γ_1 ' which is thicker compared to β_1 has twins within the martensitic variants, which can easily transform, leading to a decrease in the transformation temperatures of the alloys. The optical micrographs of the alloys S4 and S5 [Fig5 (d) and Fig.5 (e)] show coarse martensitic plates with twins within them. Since coarse γ_1 ' martensite can smoothly transform, it further lowers the transformation temperatures at higher aluminium contents.

The optical micrograph of the alloy S6 [Fig.6 (a)] shows predominantly β_1 ' martensite with slightly coarser plates when compared with that for alloy S2, even though the aluminium content is higher. This shows that the addition of iron has brought a change in the morphology of the martensite formed. In the alloys S7 [Fig.6 (b)] and S8 [Fig.6(c)] with higher iron content, a mixture of coarse γ_1 ' martensite and thin β_1 ' martensite are formed [10-12].

4. Conclusions

The influence of aluminium content (in the range of 10-13 wt %) was studied in Cu-Al-Fe alloys. It is found that increasing the aluminium content decreases the transformation temperatures and changes the morphology of the martensites formed. At lower aluminium contents predominantly β_1 ' martensite is formed, while at higher aluminium contents it is predominantly γ_1 ' martensite with some amount of β_1 ' martensite. The addition of iron has marginally increased the transformation temperatures and slightly altered the morphology of the martensites formed. It is aluminium that has a larger influence on transformation temperatures when compared to iron.

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