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A New Cu-Based SMA with Extremely High Martensitic Transformation Temperatures

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Abstract : A new series of high temperature copper based shape memory alloys has recently been patented. These alloys contain 8-20 wt% Al, 1-20 wt% Ag, 0-2 wt% of a minor element (preferably Co), balance copper. The martensitic start transformation temperatures of these alloys are above 200°C and, in some cases, they have good high temperature stability and may be useful in commercial applications where higher operating temperatures than those obtained from Cu-Zn-Al and Cu-Al-Ni shape memory alloys are required.

1. INTRODUCTION

The shape memory alloys which are industrially used are based upon NiTi, CuZnAl and CuAlNi to which minor elements such as Co, Zr, Ti are added to control grain growth. The NiTi and CuAlNi series of alloys can be used at temperatures up to 200°C.

Considerable interest (1-3) has been expressed in the possibility of producing a relatively cheap copper based shape memory alloy with a martensitic transformation temperature above 200°C. The present work describes the results obtained with a variety Cu-Al alloys containing Ag which show martensitic transformation temperatures well above 200°C.

2. EXPERIMENTAL METHOD

Different Cu-Al-Ag alloy composition have been obtained by melting the pure metals (99.9 %) in an induction furnace with an inert atmosphere of Ar. Some samples have been heated at 900°C for 15 minutes, quenched into water to 100°C for 1 minute and, then, cooled in water at room temperature.

Optical and scanning electron microscopy of the as-cast and heat treated specimens were carried out with an ISI SS60 (60 nm resolution) equiped with an EDS detector. Differential Scanning Calorimetry were carried out with a Mettler DSC-30, heating at 10°C/min from 25 to 500°C. Transformation temperatures were measured when a remarkable change in base line was observed.

3. RESULTS AND DISCUSSION

Table I shows alloy compositions and transformation temperatures for the alloys studied. It can be seen how the martensitic transformation temperatures are, in all cases, higher than 200°C.

Table I. Cu based alloy composition (wt%) and transformation temperatures (°C).

COMPOSITION			TRANSFORMATION TEMPERATURES			
Al	Ag	Co	M_s	M_f	A_s	A_f
10.9	1	--	245	135	290	380
10.7	3	--	285	140	245	475
9.8	2.7	--	376	230	281	476
9.7	3.2	--	274	194	306	369
11.2	3.8	0.7	264	164	309	454
12.8	4	--	251	186	281	382
12.8	6	--	230	139	277	441
10.1	14	--	266	157	273	402
11.3	14.9	--	300	201	289	450

Figures 1 and 2 show the DSC curves obtained for the alloys having 11.2 wt% Al, 3.8 wt% Ag and 0.7 wt% Co (Figure 1) and 9.7 wt% Al and 3.2 wt% Ag (Figure 2). Similar alloys with higher Ag content exhibit a DSC curve as is shown in Figure 3 (11.3 wt% Al, 14.9 wt% Ag).

The M_s transformation temperatures were found to change from 230 to 376°C which implies a significant increase in comparison with conventional Cu-based shape memory alloys. The enthalpy released during heating or cooling is about 10-12 J/g, higher than that found for Cu-Zn-Al alloys. However, the enthalpy released during the transformation for alloys with a higher Ag content is only between 6 and 9 J/g.

The martensitic and reverse transformation take place during an average temperature interval of 100-150°C, hysteresis (A_f - M_s) takes also place in the same interval temperature but in some cases (12.8 wt% Al, 6 wt% Ag) an interval of 211°C was found.

Figure 4 shows the martensitic structure of the as-cast alloy containing Co. In this case, the cooling is enough to promote martensitic transformation. However, for all the other alloys, the as-cast structure does not show martensitic transformation, as can be seen in Figure 5, corresponding to the alloy with 9.8 wt% Al and 2.7 wt% Ag. The presence of hypoeutectoid α_1 (fcc) Cu-rich solid solution is found at the grain boundaries, as is to be expected from examination of the ternary equilibrium diagram (4). When heating the alloy at 900°C, it becomes ß which then transforms martensitically on quenching to 100°C, Figure 6.

Other phases are present on increasing the Ag content in the alloy. Thus, the alloy having 11.3 wt% Al and 14.9 wt% Ag has a martensitic structure, after heat treatment, with the presence of the Ag-rich solid solution α_2 (f.c.c.) and the γ (cubic phase) surrounding α_2 , as can be seen in Figure 7. The presence of these phases do not, substantially, change the martensitic transformation temperatures. The small transformation enthalpy found in this alloy is due to the fact that there is less material to transform martensitically.

4. CONCLUSIONS

1.- The Cu-Al-Ag alloys exhibit martensitic transformation temperatures above 200°C, with an enthalpy about 10-12 J/g.

2.- On increasing the Ag content α_2 and γ phases appear decreasing the enthalpy obtained during transformation, but they do not affect the martensitic transformation temperatures.

5. ACKNOWLEDGEMENTS

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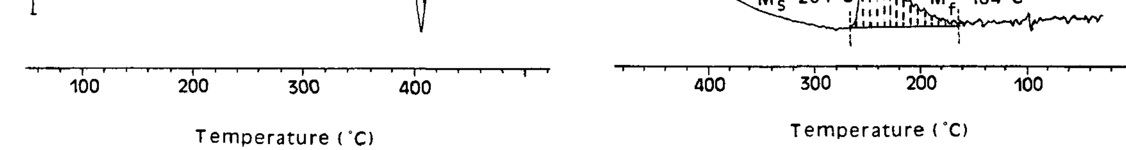

a) b)

Figure 1 a) and b). DSC curves of the sample with a chemical composition of 11.2 wt% Al, 3.8 wt% Ag and 0.7 wt% Co, balance Cu.

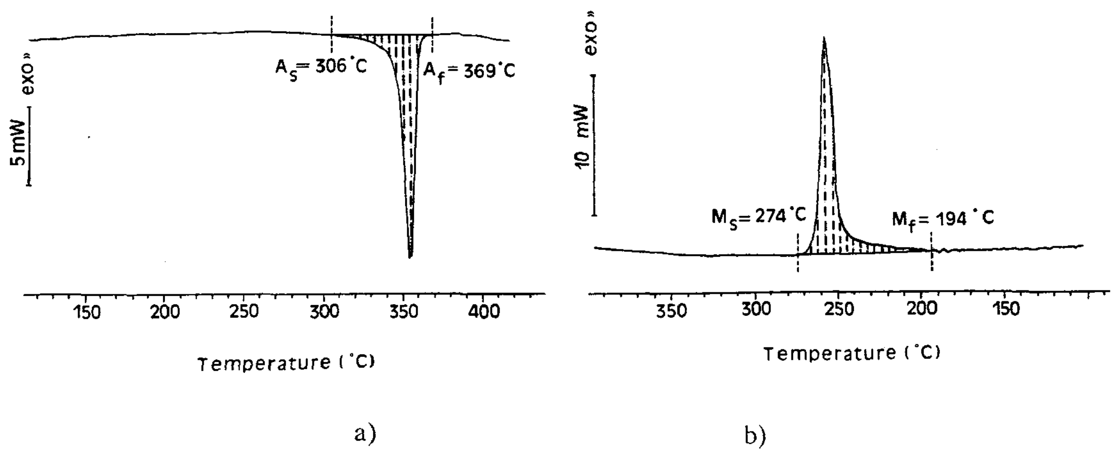

Figure 2 a) and b). DSC curves of the sample with a chemical composition of 9.7 wt% Al, 3.2 wt% Ag, balance Cu.

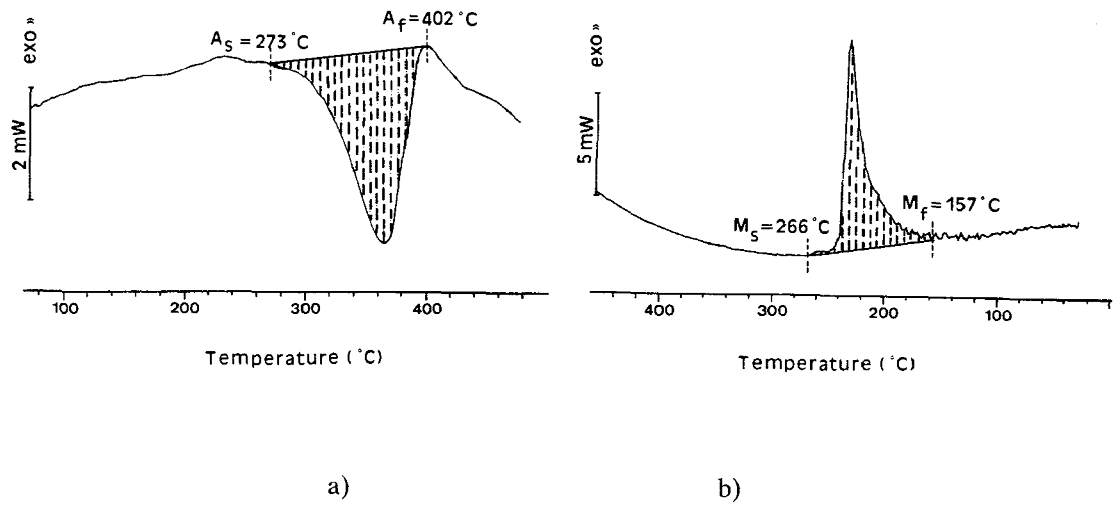

Figure 3 a) and b). DSC curves of the sample with a chemical composition of 11.3 wt% Al, 14.9 wt% Ag, balance Cu.

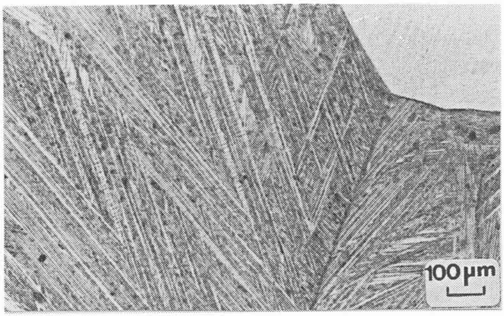

Figure 4. Martensitic structure of the alloy with chemical composition 11.2 wt% Al, 3.8 wt% Ag and 0.7 wt% Co, balance Cu.

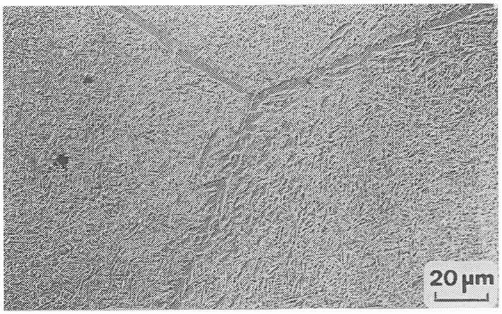

Figure 5. As-cast structure of the alloy with 9.8 wt% Al and 2.7 wt% Ag, balance Cu.

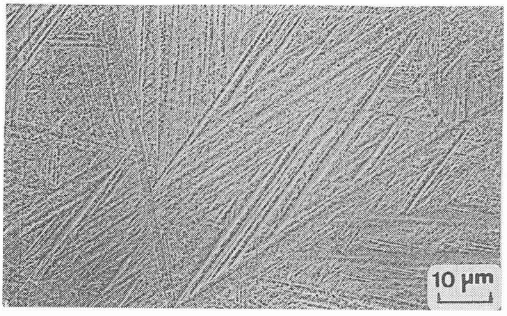

Figure 6. Martensitic structure after thermal treatment of the alloy with 9.8 wt% Al, 2.7 wt% Ag, balance Cu.

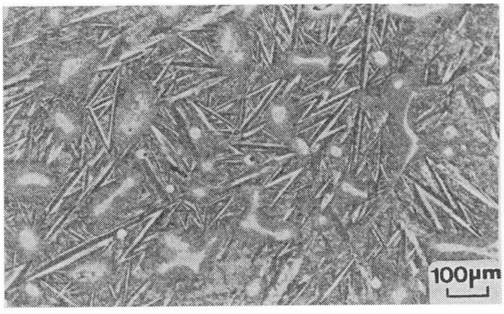

Figure 7. Martensitic, α_2 and τ structure of the Cu-11.3 wt% Al-14.9 wt% Ag after thermal treatment.