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Stable phase formation in a 85.67 wt.% Cu- 9.9 wt.% Al- 4.43 wt.% Ni shape memory alloy

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Abstract. 85.67 wt.% Cu- 9.9 wt.% Al- 4.43 wt.% Ni shape memory alloy has been studied. Polycrystalline specimens have been quenched, into water, after heat treatment at high temperature and followed by two successive runs from room temperature to 923 K and inversely. The microstructural and thermodynamic studies presented in this work have been performed using DSC (Differential Scanning Calorimetry), X-ray diffraction analysis at a variable temperature and TEM (Transmission Electron Microscopy) analysis. Stable phase precipitation of AlNi type was observed to appear in this alloy.

Keywords: Martensitic transformation; Shape memory alloys; AlNi precipitation.

1. Introduction

Shape memory alloys constitute an important group of smart materials. Among these materials the Cu-Al-Ni system offers the best potential for high temperatures applications (near 493 K) [1,2], it presents an advantage over Cu-Zn-Al and Ti-Ni alloys where their maximum working temperature is around of 373 K [3]. Cu-Al-Ni system is known to have at high temperature a V-shaped single phase field which contains the stable disordered cubic β phase. The martensitic transformation of β phase is responsible for the shape memory properties exhibited by Cu-Al alloys. During a decrease of the temperature at quenching, the disordered β stable phase undergoes two successive ordering processes [4], and the resulting phase at room temperature has a $L2_1$ cubic order [5]. Closer to the β single field phase, we have the existence of the α and γ_2 phases. The γ_2 phase appears during heating as a primary precipitation previous to the eutectoid reaction $\beta \rightarrow \alpha + \gamma_2$ [6], the crystallographic structure of this phase is described as a binary Cu_9Al_4 structure in Cu–Al–Ni [7] with a cubic cell parameter equal to 8.7039 Å. The α phase is a disordered cubic phase (a=3.682 Å) with a space group with very low aluminium and nickel content [8,9]. A Cu-Al-Ni alloy with an eutectoid composition exhibits the same particularities of the binary Cu-Al alloy. In fact, a slow cooling from the β high temperature phase gives rise to a lamellar eutectoid mixture ($\alpha + \gamma_2$), at a temperature lower than 840 K.

The purpose of the present work was to study the influence of high proportion of nickel , on the microstructural and thermodynamical evolutions, during heating- cooling double thermal cycles, from room temperature to 923 K and inversely.

2. Experimental procedures

Polycrystalline samples of Cu-Al-Ni with a nominal composition of Cu- 9.9 wt.% Al- 4.43 wt.% Ni (Cu- 20.5 at.% Al- 4.21 at.% Ni) have been used. The samples were annealed at 1123 K for 15 min and quenched in a room temperature water to obtain the β phase ($L2_1$ cubic order). DSC measurements were performed on several samples under an argon atmosphere. These heat treatments, consisting of two successively heating-cooling

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cycles, were done inside the DSC equipment under a rate of 5 K/min in the temperatures range (298-1123 K), with a holding time of a few minutes at high temperature. The phases formed were determined based on the electron probe microanalysis (EPMA) compositional measurement, XRD analysis, at variable temperatures, using the Cu Kα radiation. Finally, a transmission electron microscopy (TEM) study was performed using of a Philips CM20 TEM operating at 200 kV. The thin foils were prepared, polished mechanically, and electropolished to electron transparency using a solution of perchloric acid and acetic acid.

3. Results and discussion

The quenched structure exhibits a biphase structure formed by the martensitic β' phase and the α phase (see Fig.1). DSC thermograms Fig.2, show on heating for the first run an exothermic evolution called (A) linked to the precipitation of AlNi phase [11,12] with a calculated energy of 3.71 J/g. The next transformation, evolution (B) (7.75 J/g), corresponds to the reverse transformation of the martensite β' to an intermediate metastable β phase. This latter evolution is followed by the exothermic evolution (C) (4.09 J/g), which corresponds to the formation of the equilibrium phases ($\alpha + \gamma_2$) [13]. At around of 843 K, it appears a new endothermic evolution (8.85 J/g), called (D), which is relative to the formation of the higher stable β phase via the dissolution of γ_2 phase and a part of α phase. Also for this transformation, it is noticed the disappearance of AlNi phase.

With respect to the cooling, we observe just only an exothermic evolution (E), which corresponds to the decomposition of β phase into equilibrium constituents ($\alpha + \gamma_2$) with energy of 10.5 J/g and formation of AlNi phase. For the second run of heating, the thermogram shows only an endothermic evolution ($\alpha+\beta$), with a narrow domain of the transformation (14.06 J/g). As it can be seen, the thermogram of cooling is similar to the first one.
In order to confirm the different evolutions, Figs.3 and 4 provide different X-ray diffraction patterns during heating and cooling respectively. During cooling (at 802 K) we can see, for 50% of transformation, a peak relative to the β phase which disappears after. At room temperature, an existence of Al_xNi_y phase, corresponding to AlNi type precipitate is revealed. It diffracts according to (110) plane. On one hand, the compositional analysis by using EPMA indicates the bright and continuous phase is the α phase (Cu- 18.5 at.% Al- 3 at.% Ni), while the dark phase is AlNi phase (Cu- 41.8 at%.Al- 41.42 at.%.Ni), see Fig.5. On the other hand, the dosage by cartography X (STEM) gives the elemental distribution inside the precipitates. It also confirms the nature of these precipitates.

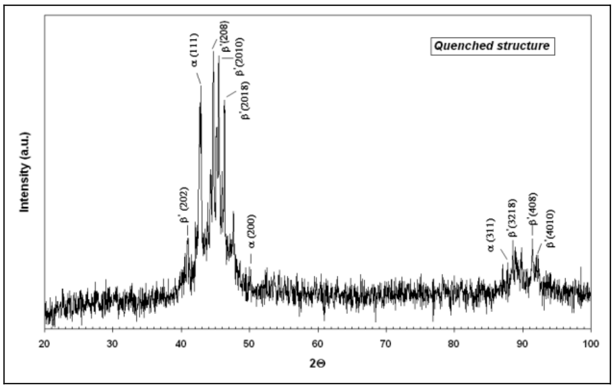

Fig.1. Quenched structure.

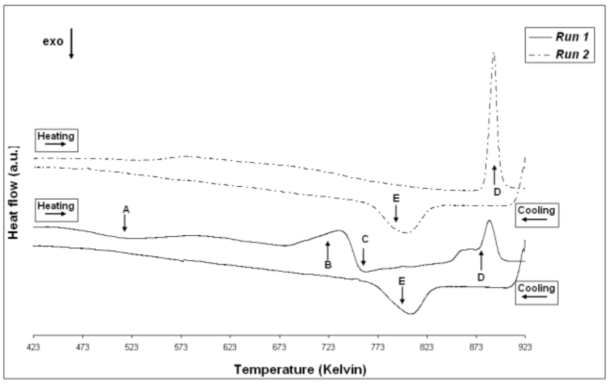

Fig.2. DSC thermograms [10].

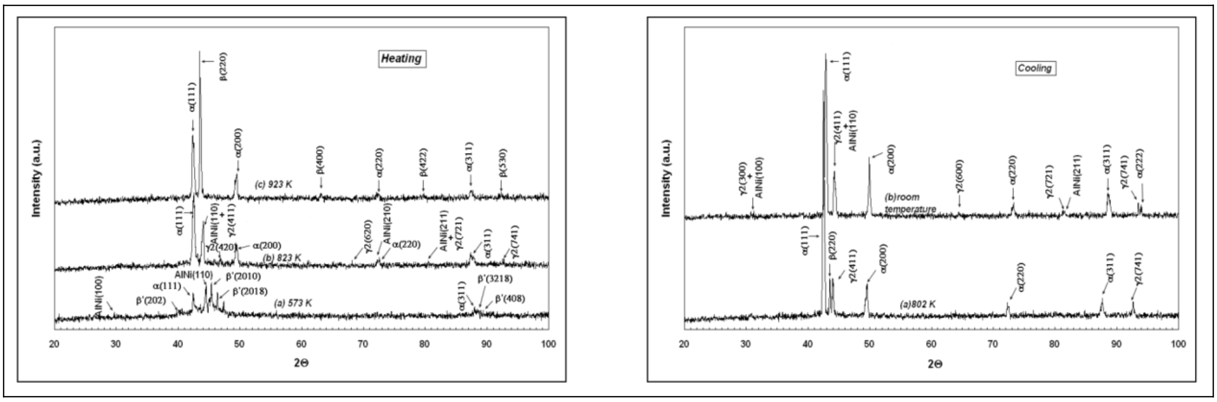

Fig.3. X-ray diffraction patterns of heating and cooling (run 1).

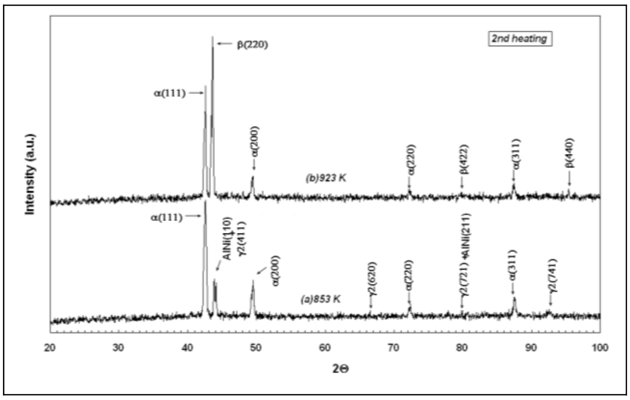

Fig.4. X-ray diffraction patterns of heating (run 2).

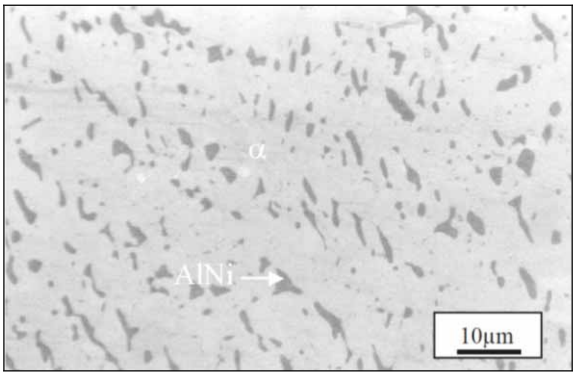

Fig.5. BEI micrograph after the second run.

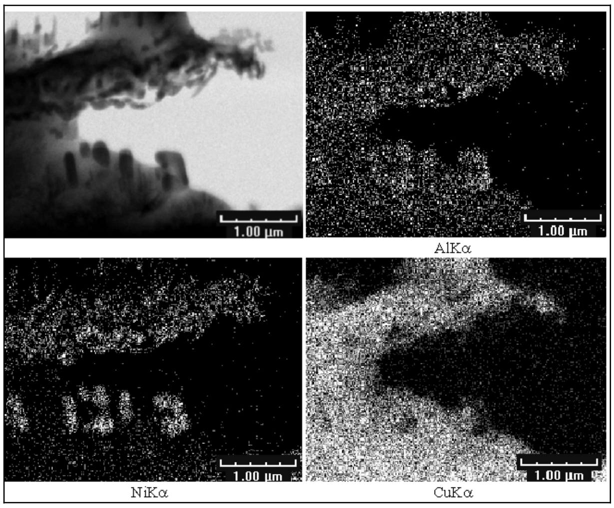

Fig.5. X-cartographies.

4. Conclusion

The following concluding points can be drawn from our experimental results as follows:

- Precipitation of a very stable AlNi phase, result confirmed by XRD, EPMA and STEM analysis.
- During a second heating, the exothermic evolution called (A) linked to the precipitation of AlNi phase does not appear.

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