A structural-morphological study of a $Cu_{63}Al_{26}Mn_{11}$ shape memory alloy

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ABSTRACT

By means of DSC, three transformations occurring on heating up to 873 K, of a martensitic $Cu_{63}Al_{26}Mn_{11}$ Shape Memory Alloy (SMA) in hot pressed and homogenized state, were revealed. The assumed precipitation of α-phase, accompanied by an exothermic reaction, was ascertained by SEM mapping. SEM micrographs revealed preferred orientation tendencies for the α-phase precipitates, inside the grains which became more prominent along grain boundaries.

Keywords: shape memory alloys, martensitic transformation, precipitates, differential scanning calorimetry, scanning electron microscopy, microstructure, morphology

1. INTRODUCTION

Cu–Al–Ni shape memory alloys (SMAs) represent one of the systems that have become commercially available due to their relatively low cost and thermoelastic character of martensitic transformation [1]. Common alloys contain (10-14) Al – (2-4) Ni – bal. Cu (hereafter all chemical composition will be in mass. %) and are grain refined with Mn, B, Ce, Co, Fe, Ti, V, and Zr [2]. In Cu–Al–Ni-based SMAs up to four martensites (α'_1, β'_1, β''_1 and γ'_1) can be observed along with an ordered parent phase, also called austenite (β_1 based on Cu_3Al) and three equilibrium phases (α, NiAl and γ_2, based on Cu_9Al_4) [3]. At rapid cooling β_1 (DO_3) austenite usually transforms into γ'_1 (2H orthorhombic) thermally induced martensite, while the other three above mentioned martensites are stress-induced within specific ranges of chemical compositions and applied stress levels [4]. At slow cooling, in equilibrium state, β_1 ordered austenite undergoes an eutectoid decomposition, into $\alpha + \gamma_2$, [5]. When Cu-Al-Ni based SMAs, with thermally induced martensite structure, were subjected to heating, up to four solid state transitions were observed [6]. Firstly, the reverse transformation of γ'_1 martensite to β_1 (DO_3) austenite was produced in a single or a double stage [7]. Secondly, exothermic precipitation of equilibrium α or γ_2 phases occurred from β_1 austenite, at lower or higher aluminum contents, respectively [8, 9]. Thirdly, β_1 (DO_3) austenite became less ordered and turned to β_2 (B2) austenite and finally a second order-disorder transition took place, which transformed β_2 (B2) austenite into completely disordered β (A2) austenite [10]. In previous reports the influence of γ_2 phase precipitation on shape memory behavior of Cu-Al-Ni-Mn-Fe SMAs was analyzed and no major changes were detected in the subsequent reversion of martensite to austenite, after the quenching of an alloy in which hard γ_2-phase had precipitated [11]. Moreover, no orientation relationship was revealed between austenitic matrix and precipitates although the alloy under study experienced shape recovery degrees higher than 96 % [12]. On the other hand, in Cu-21.57 Zn-7 Al SMA the precipitation of copper-rich equilibrium α-phase did not cause total degradation of shape memory phenomena, even if it shifted critical temperatures of reversible martensitic transformation [13].

Considering the above observations, the present paper aims to bring more evidence on the structural-morphological connection between α-phase precipitates and matrix in a Cu-Al-based SMA.

2. METHODOLOGY

After casting, hot forging (60 % thickness reduction at 973 K) and homogenization (1173 K/ 8·3.6 ksec/ air), specimens were prepared from a $Cu_{63}Al_{26}Mn_{11}$ SMA for differential scanning calorimetry (DSC), and scanning electron microscopy (SEM) studies, as previously described [12].

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DSC measurements were done on a 2920 Modulated DSC TA INSTRUMENTS unit, with a heating rate of 10 K/min. SEM micrographs were recorded by means of a SEM – VEGA II LSH TESCAN scanning electron microscope, coupled with an EDX – QUANTAX QX2 ROENTEC detector.

3. RESULTS AND DISCUSSION

3.1 DSC thermogram

Fig. 1 presents a typical DSC thermogram recorded during the heating $Cu_{63}Al_{26}Mn_{11}$ SMA specimens, emphasizing three solid state transitions.

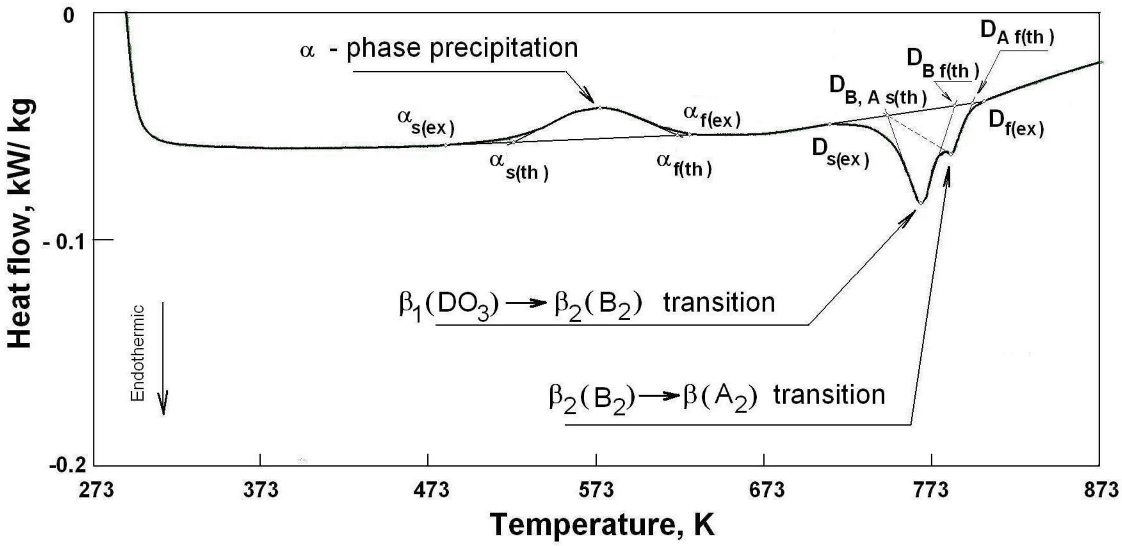

Fig. 1 Typical DSC thermogram recorded during the heating of hot forged (60 % thickness reduction at 973 K) and homogenized (1173 K/ 8·3.6 ksec/ water) $Cu_{63}Al_{26}Mn_{11}$ SMA revealing three solid state transitions.

Since martensite reversion was not detected, and no signs of martensite instantaneous stabilization were noticeable [14], it is assumed that initial structure may be rather austenitic than martensitic. In addition, considering that Al content is rather low, α-phase precipitation is expected to occur. On the thermogram the corresponding start and finish critical temperatures were determined for both experimental and theoretical transformations, designated with subscripts $_s$ and $_f$ as well as $_{ex}$ and $_{th}$, respectively. For α-phase precipitation, located around 575 K, these values were: $\alpha_{s(ex)}$ = 483 K; $\alpha_{s(th)}$ = 524 K; $\alpha_{f(th)}$ = 621 K and $\alpha_{f(ex)}$ = 629 K, while specific enthalpy emission was between 5.48 and 7.34 kJ/ kg. Between $D_{s(ex)}$ = 712 K and $D_{f(ex)}$ = 804 K two disordering transition occur. Theoretical critical temperatures for β_1 $(DO_3) \rightarrow \beta_2$ (B2) order-disorder transition were: $D_{Bs(th)}$ = 747 K and $D_{Bf(th)}$ = 787 K and for β_2 $(B_2) \rightarrow \beta$ (A2) order-disorder transition were: $D_{As(th)}$ = 747 K and $D_{Af(th)}$ = 797 K. These results suggest that both transitions start at the same temperature, 747 K [15]. On the other hand, previous DSC results obtained on Cu-Al based SMAs have shown that eutectoid reaction also occurred on heating, at about 770 K [7]

3.2 SEM observations

The typical SEM micrographs of the alloy under study, after being subjected to 873 K heating and air quenching, are shown in Fig. 2. As predicted from Fig.1, α-phase precipitation obvious occurred, both along grain boundaries and inside the grains. Grain boundary precipitation caused primary coarse precipitates while the precipitation inside the grains caused finer secondary-phase particles. Primary α-phase precipitates display preferred orientation tendencies in neighboring grains, with intersection angle about 120^0. Their width is about several μm while their length is between 20-30 μm. Secondary α-phase precipitates are much finer, with width less than 1 μm and are mode dense. The general aspect of the matrix suggests that it represents an eutectoid [2].

In order to better reveal the morphology of α-phase precipitates and to detect chemical composition fluctuations, between the component metallographic phases, a detail of the of primary α-phase precipitates, from Fig. 2(b), is shown in Fig. 3(a) and a phase image is illustrated in Fig. 3(b) as determined by means of SEM electron microprobe.

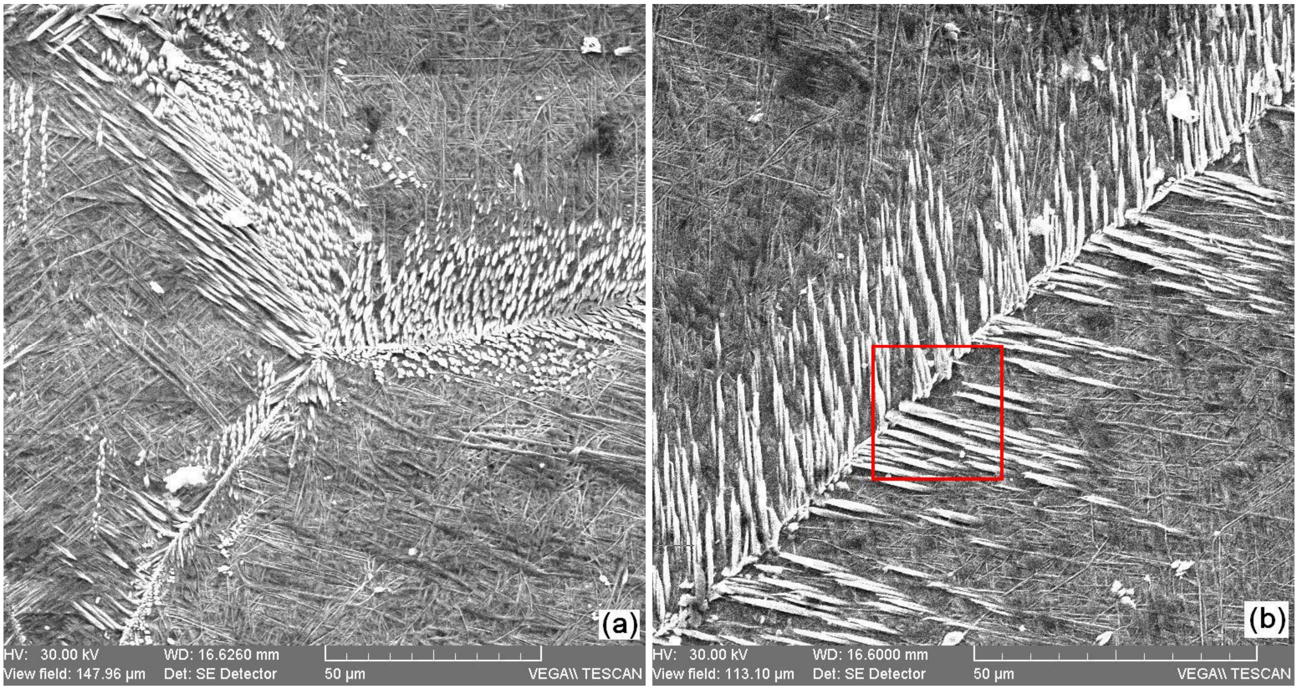

Fig. 2 Typical SEM micrographs of hot forged (60 % thickness reduction at 973 K) and homogenized (1173 K/ 8·3.6 ksec/ water) $Cu_{63}Al_{26}Mn_{11}$ SMA after 873 K heating and air quenching, etching with 30 % HNO_3 aqueous solution: (a) primary and secondary α-phase precipitates; (b) enlarged view of α-phase precipitates.

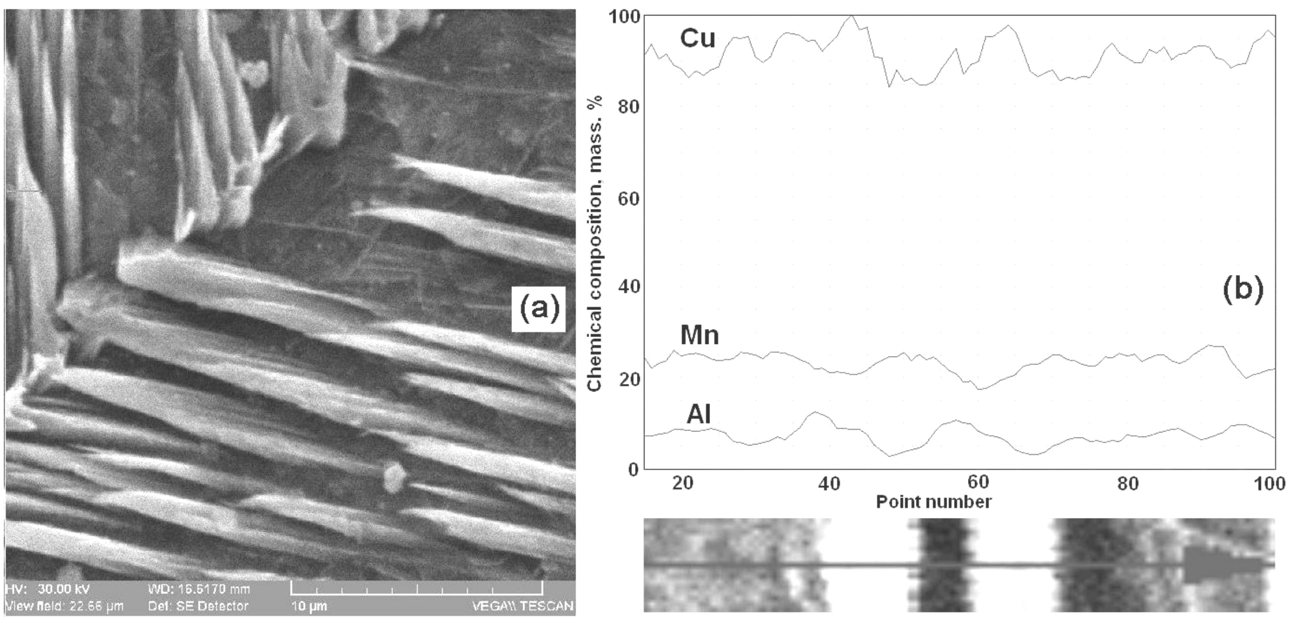

Fig. 3 Electron microprobe observations on hot forged (60 % thickness reduction at 973 K) and homogenized (1173 K/ 8·3.6 ksec/ air) $Cu_{63}Al_{26}Mn_{11}$ SMA after 873 K heating and air quenching, etching with 30 % HNO_3 aqueous solution: (a) magnified detail of α-phase precipitates, from Fig. 2(b) (b) chemical composition variation on α-phase and matrix.

The detail from Fig. 3(a) reveals the fact that, after etching α-phase appears in relief as compared to the matrix. The composition image from Fig. 3(b) shows higher Cu-contents and lower Al-contents, as compared to the matrix, at the corresponding level of α-phase precipitates. These results agree with theoretical chemical compositions of α-phase, which is copper-based and of the matrix, which is based on Cu_3Al, therefore richer in Al but poorer in Cu.

4. CONCLUSIONS

A $Cu_{63}Al_{26}Mn_{11}$ shape memory alloy with ferromagnetic properties [16] was analyzed in hot pressed and homogenized state, revealing austenitic structure. During heating to 873 K, exothermic α-phase precipitation occurred with 5.48 - 7.34 kJ/ kg specific enthalpy emission. The structure, analyzed after heating to 873 K and subsequent air cooling, revealed the formation of primary and secondary precipitates which, by electron probe phase imaging were ascribed to α-phase. Primary precipitates were formed along grain boundaries while secondary precipitates had very large densities and were observed only inside the grains. The results suggest that rather eutectoid decomposition than forward martensitic transformation occurred during post-precipitation cooling from 873 K.

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