STRUCTURAL STUDY OF EXTRUDED CuAl13Ni4 SHAPE MEMORY ALLOY

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Abstract: This paper presents a structural study for a copper based shape memory alloy. The behavior of CuAl13Ni4 alloy is evaluated by DSC, electrical resistivity, X-ray diffraction and SEM. On cooling, the martensitic transformation takes place from the ordered structures to long period two layered structure. The crystalline phase transformations of these alloys are very sensitive to the heat treatments, deformation degrees and also to the undesired aging effects. In particular, the study has been made on the CuAl13Ni4 shape memory alloy samples after hot extrusion, quenching and aging in martensitic state.

1. INTRODUCTION

The studies of Cu-based ternary SMAs have been generally on single crystals but only few publications on polycrystalline alloys were found [1]. This paper presents a structural study for a Cu-based SMA. The behavior of CuAl13.01Ni4.0 alloy is evaluated by XRD. On cooling, the martensitic transformation takes place from the ordered structures to long period two layered structure. The crystalline phase transformations of these alloys are very sensitive to the heat treatments, deformation degrees and also to the undesired aging effects. In particular, the study has been made on the CuAl13Ni4 SMA samples after hot extrusion, quenching and aging in martensitic state.

Polycrystalline Cu-Al-Ni SMA’s are a considerable cheaper alternative to classical Ti-Ni alloys. They are more resistant to degradation of functional properties due to undesired aging effects than Cu-Zn-Al SMA’s [2] and may work at a higher temperature (near 473 K).

The characteristic temperatures of martensitic transformation Cu-Al-Ni alloys are in the range from 72K to 473K and depend on aluminum and nickel content. The following empirical equation shows the stronger influence of Al content and estimates the M1 temperature [4]:

\[ M_1 (K) = 2293 - 45 \times (\text{wt\% Al}) - 134 \times (\text{wt\% Ni}) \] (1)

Depending on alloy composition and heat treatment, Cu-Al-Ni SMA’s may transform from high temperature parent phase [1] (DO3) to two types of thermal induced martensite at low temperature: β1’ (18R), for 11%-13% Al, or γ1’ (2H), for more than 13% Al. In alloy compositions near 13%M, two martensites can coexist [4].

The investigated alloy in this paper Cu-13Al-4Ni (wt %) lies in the region of the phase diagram where β1’ and γ1’ thermal induced martensites may coexist. The effect of nine months aging in extruded state, annealing time and temperature, thermal cycling of transformation temperatures was studied on a polycrystalline sample with 13 %wt Al, by differential scanning calorimetry (DSC), electrical resistivity (ER), X-ray diffraction (XRD), scanning electron microscopy (SEM).

2. EXPERIMENTAL PROCEDURES

The polycrystalline Cu-13 Al-4Ni (wt %) alloy was elaborated by classic melting in a tilting induction furnace from Dunarea de Jos University of Galați. The samples were extracted from 9 months aged hot extruded wires 4 mm diameter and 145 mm length. The samples were machined with different geometries for following tests. For each test we studied the same samples after extrusion and a subsequent quenching. The experiments for quenched samples comprised heat treatment using a vertical furnace (air environment) holding at 1123 K, 1173 K, 1203 K for 30 minutes. The samples were cut from wires (4mm diameter) and were introduced in the furnace at the holding temperature for annealing. After solidification, the specimens were immediately quenched in ice water.

2.1. DSC

For DSC measurement were used small pieces weighting less than 0.100g. The calorimetric experiments were performed by using SETARAM 92 instrument in the temperature range between 223 K and 523K (cooling by liquid nitrogen) with heating and cooling rates of 0.35K/s. Endothermic and exothermic peaks on DSC profiles were taken from two sets of experiments:

- One thermal cycle was performed for each condition of heat treatment;
Ten thermal cycles were performed for sample annealed at 1123K for 30 minutes and rapidly quenched in iced water.

2.2. XRD analysis

The XRD analysis was run on a Rigaku (Cu sealed tube) at room temperature using 20 mm x 2 mm x 1 mm dimension samples. The peaks were observed between 10° and 90° value for 30. The acquisition time was 10 point. The radiation used was Cu-Kα. The divergence, anti-scatter and receiving slits were set at 0.40, 0.40, and 0.15 mm, respectively.

2.3. Electrical resistivity

Electrical resistivity was measured using a home made four-point probe based connected with a power supply. Thermo Electron COOP DC 50-K40. Samples of 71.25mm x 3.15mm x 1.2mm were used to analyze the transformation temperatures and the hysteresis involved. Thermal cycles were performed between room temperature (below Mf) and 423K (above Ar) on heating, and between 423K and 253K on cooling, for all quenched samples. These thermal cycles were applied to 9 months aged, as well as 1123K, 1173K, and 1203K annealed/operated specimens.

Prior to the DSC, EIT and XRD experiments all the samples were submitted to the chemical etching (1:1 HNO3 in H2O) for 13 minutes in order to remove the layer deformed by the cutting operation as well as the oxide.

2.4. SEM

SEM micrographs were carried out in a ZEISS DSM 962 Scanning Microscope. The surfaces of the samples were first mechanically polished using conventional procedures and etched with FeCl3. Also SEM images were observed in cross sections from tensile test specimens.

3. RESULTS

3.1 DSC analysis

Figure 1 shows the transformation temperatures (Aγ, As, Ms, and Mf) as a function of annealing temperature for one cycle performed in each condition of heat treatment.

Figure 1. The transformation temperatures at Cu-13 Al-4Ni (wt %) for different annealing temperatures

Figures 2-3 show the DSC curves plotted and the transformation temperatures (Aγ, As, Ms, and Mf) for ten thermal cycles performed on a sample annealed at 1123K using 0.25K/s cooling and heating rate.

The transformation temperatures were calculated from the DSC curves associating the start and finish temperatures to 1% and 99%, respectively.

3.2. XRD analysis

Figure 4 compares the XRD patterns for a sample aged for 9 months at room temperature after extrusion of a sample annealed at 1123K for 1.8k.

Figure 2. The DSC curves plotted for ten thermal cycles performed on a sample annealed at 1123K

Figure 3. The transformation temperatures of the sample annealed at 1123K (cooling and heating rate 4.8K/s) vs. thermal cycles number

3.3. Electrical resistivity analysis

Figure 5 shows electrical resistivity on plate shaped samples sulphidized at 1123K and 1153K.

3.4. Tensile tests

Mechanical behavior was studied for tensile test until fracture on the samples annealed at 1123K, 1173K and 1223K all of them immediately quenched in iced water (Fig. 6).
Figure 4 The room temperature XRD patterns of plate samples: aged (1), quenched (2).

Figure 5 ER curves at different annealing temperatures.
3.5. SEM micrographs

Figures 7-8 present the SEM images on aged and quenched alloy (failure surface and etched surface).

Figure 7 SEM micrographs of Cu-13 Al-4Ni (wt %) in fracture surface aged (a) and annealed at 1123 K and quenched (b).

Figure 8 SEM micrographs of Cu-13Al-4Ni (wt %) mechanically polished and etched with FeCl₃ aged (a) and quenched from 1123K (b).

4. DISCUSSION

4.1. Phase transformation and critical points

The DSC plot of aged hot extruded alloy shows no phase transformation. After quenching, the samples showed typical characteristics of thermoclastic martensitic transformation.

Concerning the influence of annealing temperature on critical points position (figure 1), As and Af temperatures remain almost constant for the three annealing temperatures studied (1123, 1175 and 1203 K). Ms and Mf increases with increasing annealing temperature, reaching 472 K for annealing at 1203 K. This observation is important because one strong point for this polycrystalline Cu-13 Al-4Ni alloy is the high service temperature (near 475 K [19]) inaccessible for Ni Ti alloys.

Figure 2 shows of 10 DSC cycles (heating / cooling between 223 K and 522 K). Endothermic and exothermic thermal peaks values are approximately constant, from 225 W/g to 250 W/g, showing a relatively good thermal stability of the alloy on repeated heating / cooling cycles.

When thermal cycling is complete (direct and reverse martensitic transformation) a large number of dislocations in martensitic phases are produced. That results in an increase of both Ms and Af temperatures in parallel.

The transformation temperatures do not change significantly during the successive 10 thermal cycles tested: Af increased only 4 K and Mf increased 12 K. The D03
parent phase order, in fact, generate a much lower density of defects than B2 ordered structure does in Ni-Ti SMAs, giving a relatively good stability during thermal cycling.

Electrical resistivity reveals how Ms temperature is affected by precipitation and ordering upon aging the parent phase of Cu-Al-Ni SMAs. The SMAs with lower Ni content are susceptible to decomposition and thus the precipitation from the β phase proceeds upon aging, as seen from the increase of electrical resistivity. For the 9 months aged sample, the ER increases linearly within the temperature range tested, showing that there is no phase transformation.

At 1123K solubilized sample there is a phase transformation that starts around 353K, the resistivity starts to decrease until 376K when the phase is finished and the resistivity has the tendency to increase. On cooling a reverse phase transformation takes place.

For the specimens solubilized at 1175K and 1203K we observed phase transformation on heating and on cooling only that on 503K. A decrease of resistivity appears between the first cycle and the other two (fig.5).

4.2. Structural constituents and morphologies

The XRD patterns performed at room temperature show the presence of α-CuAl, Al2Cu2Ni, CuAl2, NiAl. All constituents detected in the range from 10° to 90° belong to the ternary system Cu-Al-Ni. The fracture surface after tensile tests showed a considerable difference between the aged and the annealed/quenched samples (Fig. 7). The aged hot extruded samples with a large grain size, well defined contribute to the stress concentration. SEM micrographs present the same difference between aged and quenched alloy microstructure after cycling with Pct. The aged structure is a distorted one. In the annealed/quenched state, the samples usually transform into two typical martensite configuration, 18R (β1) and 2H (γ1) long period stacking order (LPSO). Figure 8 confirms the coexistence of all types of martensite structures in the investigated samples. The structure of 18R martensite variants is a monoclinic formed typical trigonal morphology. These results are coherent with ones obtained from the XRD patterns. The 2H martensite appears as coarse variants [2].

4.3. Mechanical Behavior

The tensile test was performed at room temperature on 4 mm diameter extruded wires for aged state and machined samples for annealed and quenched state. In the case of the 9 months aged sample, the ultimate tensile stress (UTS) value is 579 MPa. This mechanical parameter increases significantly for the sample annealed at 1123 K (1234.0 MPa) due to the high mechanical strength of the martensitic phases. On the other hand figure 6 shows that the UTS decreases with increasing annealing temperature. This fact is explained by the coarse grained structure. In this alloy, high annealing temperatures give rise to an accenrated grain growth and, finally, brittleness.

Mechanical failure of polycrystalline Cu-Al-Ni alloys is normally caused by high shear stress concentrations at grain boundaries resulting in a brittle intergranular cracking. High shear stress concentrations appear because of high elastic anisotropy and consequently incompatible deformations of adjacent grains [11].

5. CONCLUSIONS

Aged and annealed/quenched Cu-13Al-4Ni (wt %) SMA samples were investigated by DSC, XRD, ER, tensile test, and SEM, techniques. The results are summarized as follows:

1. After solubilization followed by quenching the Cu-Al-Ni showed phase transformations that are typical of the Shape Memory Effec.

2. The investigated samples showed a good stability of the transformation temperature after thermal cycling (up to 10 cycles).

3. During tensile testing, the fracture occurred very early, most probably due to the porosity of the material.

4. The electrical resistivity (thermal cycling) tests have shown that there is a gradual structural evolution during heating up to 413K that results in a gradual decrease of the electrical resistivity.

5. SEM and XRD observations have shown simultaneous presence of two martensite types phases in the same specimen, 18R (β1) and 2H (γ1) LPSO.

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6. REFERENCES


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