*International Symposium of Research Students on Materials Science and Engineering*
*December 20-22, 2004, Chennai, India*
*Department of Metallurgical and Materials Engineering, Indian Institute of Technology Madras*

# EFFECT OF COMPOSITION ON THE TRANSFORMATION TEMPERATURES OF CU-AL-NI BASED SHAPE MEMORY ALLOYS

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## ABSTRACT

Cu-Al-Ni based shape memory alloys have been developed as an alternative to the conventional Cu-Zn-Al and Ni-Ti based shape memory alloys. The main interest in these alloys from a technological point of view is their possible use at temperatures near 200°C. However transformation temperatures in Cu-Al-Ni alloys are very sensitive to variations in composition. In the present work, Cu-Al-Ni alloys of different compositions were prepared by ingot metallurgy route. After casting, the alloys were homogenized and subjected to various heat treatment operations. Martensitic transformation temperatures were obtained by Differential Scanning Calorimetry (DSC) technique. The result shows that even small composition variations in composition result in large variations (50-100ºC) in the transformation temperatures.

**Keywords**: Smart materials, Cu-Al-Ni shape memory alloys, transformation temperature.

## 1. INTRODUCTION

The martensitic transformation in Cu-Al-Ni alloys occurs from an ordered b.c.c $\beta$ phase. The high temperature $\beta$ phase has a disordered A2 structure, but upon cooling the structure goes through a nearest neighbor ordering transition and develops the B2 superlattice structure[1]. Further cooling induces next neighbor ordering and the structure eventually becomes the $DO_3$ or $L_{21}$ superlattice structure depending upon the alloy composition. All structures of martensite in Cu-Al-Ni alloy have long period stacking order (LPSO) type 3R, 9R, and 2H which corresponds to the $\alpha'$, $\beta'$, $\gamma'$ martensite respectively and depending upon the alloy composition, martensite changes from $\beta'$ to $\gamma'$ . The thermally induced martensite in Cu-Al-Ni alloy consists predominately of $\beta'$ martensite. $\gamma'$ martensites are usually found in alloys with higher aluminum content. Thus when the aluminum content increases, the transformation changes from $\beta \rightarrow \beta'$ to the $\beta \rightarrow \gamma'$ showing an intermediate concentration range where both martensites coexist and the transformation $\beta \rightarrow \beta' + \gamma'$ is observed. On the other hand, an increase of nickel content stabilizes the $\beta'$ martensite, giving place to an evolution from the mixed $\beta \rightarrow \beta' + \gamma'$ transformation to $\beta \rightarrow \beta'$ transformation. Thus an increase of aluminum content stabilizes the $\gamma'$ martensite with respect to the $\beta'$ martensite, and on the contrary an increase of nickel content produces the reverse effect[2].

## 2. EXPERIMENTAL PROCEDURE

2.1 Alloy compositions Investigated:

Raw materials of high purity were used for preparing the Cu-Al-Ni alloy. The Cu, Al, and Ni used had purities of 99.98%, 99.99%, and 99.9% respectively. The choice of the alloy compositions were based on data available in literature and the electron by atom ratio. Based on these criteria, the composition for Cu-Al-Ni in the range of 82-86 % Cu, 10.5-14 % Al, and 3-5 % Ni were selected for the study. The initial compositions used for melting of these alloys were somewhat different to account for oxidation and evaporation losses during melting. Allowances for these were estimated using data obtained from several trials.

2.2 Melting and casting procedures:

The required amounts of copper, aluminum, and nickel were weighed in a digital balance and loaded into the resistance furnace with provision for using a protective atmosphere of argon. This maintains a highly inert atmosphere within the furnace throughout the melting and thereby avoids excessive oxidation of alloying elements in the charge. The alloy was melted at 1060°C for three hours. After complete mixing, the liquid alloy was poured into a cast iron mould of dimensions 12 x 3 x 1.5 $cm^3$ and allowed to solidify. The cast samples were homogenized at 900°C for 2 hours to reduce the degree of segregation and make the composition uniform. After homogenization, the compositions of the Cu-Al-Ni shape memory alloys were determined using the spectrophotometric techniques using an optical emission spectrometer.

2.3 Characterization of shape memory alloys*:*

After homogenization of the alloys, step quenching heat treatment was given to the samples. This consisted of quenching into water bath at $100^oC$, followed by quenching into iced brine at $0^oC$. Optical microscopy was used to study the details of the microstructure, grain boundaries, twins and precipitate morphologies. Differential scanning calorimetry (DSC) was used for the determination of transformation temperatures. This was carried out using a Netzch DSC-204 calorimeter at a scanning rate of 5°C/minute. The thermo mechanical treatments and grain refinement result in the formation of new phases as well as modification of the existing phases of the alloys. The X-ray diffraction technique was used for qualitative analyses of the phases formed.

## 3. RESULTSAND DISCUSSION

The compositions of the Cu-Al-Ni shape memory alloys prepared were studied using optical emissions spectrometry (O.E.S). The compositions of the Cu-Al-Ni samples obtained are shown in Table 1. In order to study the dependence of martensitic transformation on composition of Cu–Al–Ni, these five samples with different compositions were taken and were step quenched into water bath and transformation temperatures determined.

Figure 1 (a) and 1 (b) show transformation temperature with respect to aluminum and nickel respectively. It is very clear from Fig. 1 (a) that for 10.65 % Al, no transformation temperature were obtained while for 13.07 % Al the highest $M_s$ and $M_f$ were obtained. It is seen from Figure 1 (b) that the highest transformation temperature were obtained in the case of 3.25 % Ni. At 4.04 % Ni, transformation temperature was not obtained at all. If we compare the Fig. 1 (a) and 1 (b), one sees that the highest transformation temperature was obtained at higher composition of aluminum (13.07%) while in case of nickel, higher transformation temperature were obtained at lower nickel composition (3.25 %). Thus an increase of aluminium content stabilizes the $\gamma'$

with respect to the β′, and on the contrary an increase of nickel content produces the revere effect that matches with the literature[2,3]. Thus alloy designated CAN-01 gave the highest transformation temperature.

Optical micrographs of different sample are shown in Figure 2. Figure 2 (a) shows the fully martensitic structure which is of plate like, while Figures 2 (b) and (c) shows the randomly oriented martensite. Figure 2 (d) shows the straw type structure of martensite while Figure 2 (e) does not show any martensitic structure. Figure 3 shows the XRD graph of CAN 02 sample after heat treatment, which confirms that martensite obtained is of 18R type with orthorhombic structure and the phases obtained are $Cu_3Al_2$ and CuAl respectively.

## 4. CONCLUSIONS

The transformation temperature does not show a linear dependence on amount of alloying additions. For Cu-Al-Ni alloys, the alloy with composition Cu-13.07 Al- 3.24 Ni gives the highest $M_s$ and $M_f$ temperature of 184°C and 182°C respectively while Cu-11.36 Al-4.35 Ni gives the lowest transformation temperature of 91°C and 83°C respectively. For Cu-10.65 Al-4.04 Ni alloy, transformation temperatures were not obtained.

## 5. REFERENCES

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2. Recarte V, R.B. Perez-Saez, E.H. Bocanegra, M.L.No and J. San Juan,. *Materials Science and Engineering A*, (1999) 273, (1999) 380.
3. Humbeeck J. V., *Materials Science and Engineering A*, 273, (1999) 134.

**TABLE**

Table 1. Composition of Cu-Al-Ni alloys produced by melting

| Sample ID. | Cu-Al-Ni (CAN) Composition in Wt % | | |
|---|---|---|---|
| | Cu | Al | Ni |
| CAN 01 | 83.6 | 13.07 | 3.24 |
| CAN 02 | 83.9 | 11.36 | 4.35 |
| CAN 03 | 83.9 | 11.75 | 4.14 |
| CAN 04 | 84.5 | 11.65 | 3.73 |
| CAN 05 | 85 | 10.65 | 4.04 |

# FIGURES

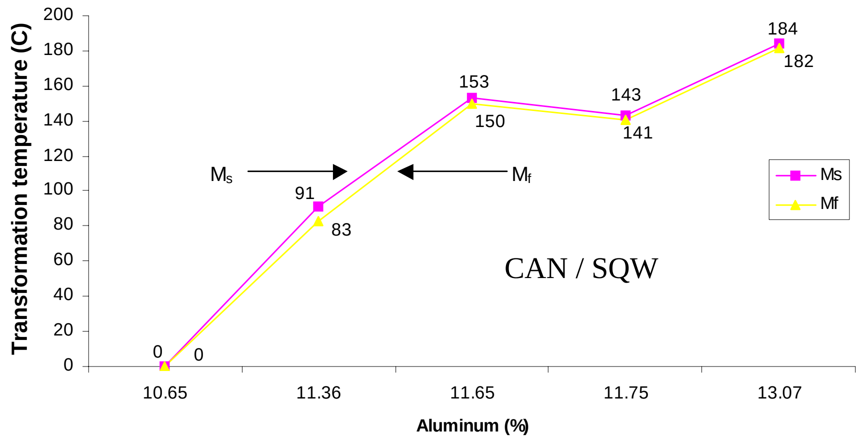



Fig. 1 (a) shows the variation of the transformation temperature with aluminum for Cu-Al-Ni specimens.

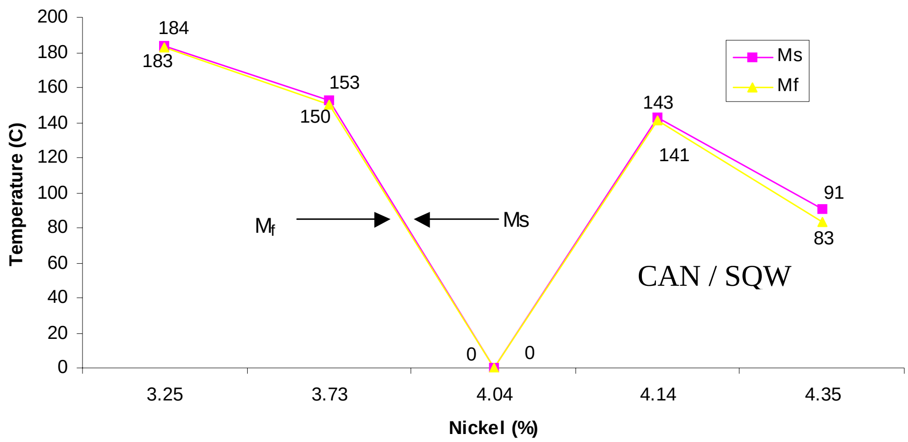
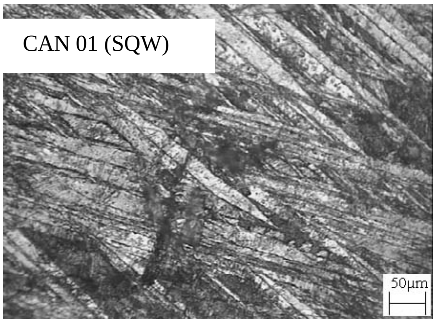
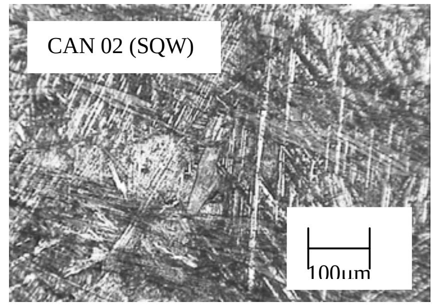


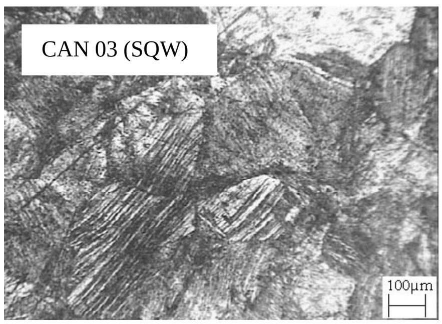

Figure 1 (b) Variation of the transformation temperatures with nickel for Cu-Al-Ni specimens.



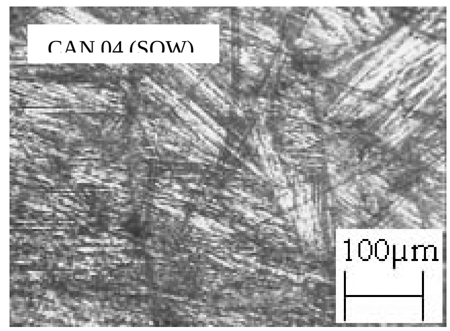

**(a) Fully martensitic structure**



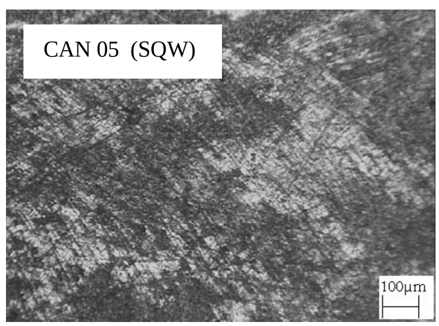

**(b) Randomly oriented martensite**




**(c) Randomly oriented martensite**




**(d) Straw type martensite**




**(e) No martensitic structure**

Figure 2 Sample micrographs of CAN samples after heat treatment showing the morphology of martensite and precipitates

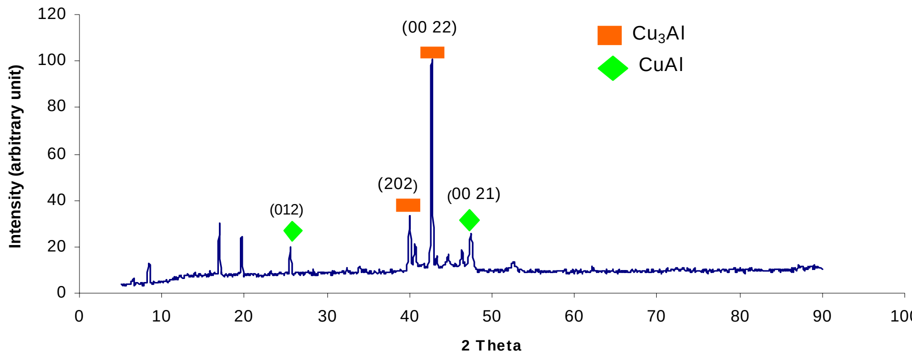



Figure 3. XRD pattern obtained from CAN 02 sample after heat treatment