# THE EFFECT OF CHROMIUM ON MICROSTRUCTURE OF CUALNI SHAPE MEMORY ALLOY

TEIXEIRA Camila A.[1], COELHO Rodrigo E.[1], LIMA Pedro C. [1], NASCIMENTO Carina S. [1], MENDONÇA Erick S. [1], SANTANA Murilo S. [1], COSTA Gabriel K. A.[2]

[1]*IFBA – Federal Institute of Education, Science and Technology of Bahia, Salvador, Brazil*
[2] *University of Brasilia - UnB, Brasilia, Brazil*

**Abstract**

In the present work, alloys with a Cu-14Al-4Ni (wt.%) composition and different content of chromium (2, 3 and 4 wt%) were casted in a plasma melting furnace, processing it two times to obtain little billets. A plasma furnace (Company-EDG, model-Discovery), with vacuum control and argon gas injection, was utilized. Posteriorly, the samples underwent heat treatment of betatization where they were submitted to a temperature of 900°C and subsequently cooled in water at -1°C. Thereafter, the samples were polished and etched with Ferric Chloride. All samples were analyzed X-ray Fluorescence, Differential Scanning Calorimetry (DSC), Scanning Electron Microscopy (SEM) and X-ray Diffraction (XRD). X-ray fluorescence measurements were carried out in a Bruker S2 RANGER, DSC experiments were under dynamic nitrogen atmosphere from -80°C up to 200°C at a heating rate of 10°C/min, and XRD experiments were from 30° to 100°. The results showed that by increasing the amount of chromium in Cu-Al-Ni alloy, presented a martensite structure with nanometrics diameters needles.

**Keywords:** Shape Memory Alloy, Effect of chromium, CuAlNi alloy

## 1. INTRODUCTION

The Shape Memory Alloy (SMA) are considered smart materials due to its capability to damp and its thermomechanical recovery when alternating between austenite and martensite stable phases. This thermomechanical recovery is influenced by many factors, such as chemical composition, structure and grain size [1]. SMAs have a vast application field in the Space/Aeronautic, in actuors and mechanical connections, in the automotive industry and biomedical area for modern proteses fabrication and surgical tools [2].

Among the various SMAs, the Copper base is one of the most attractive. Differently of NiTi, the Cu-based have relative lower costs when compared. Developed at the 1960 decade, these alloys possess the advantage of high thermical and eletrical conductivity, besides high strain rate. One of the most important Cu-based SMAs is Cu-Al-Ni, for its small hysteresis and wide operating temperature range that is up to 200°C [3].

Nevertheless, Cu-Al-Ni have some limitations, such as brittleness, due to large grain size, which has been a major prohibitive factor in their commercial utilization [4,5]. In order to refine the grain it is common to add a quaternary element [5,6]. Experiments with the addition of boron alloy materials gave the most stable and best grain refinement in spite of not having the favourable structure [7]. Thereby, the addition of a material strange to the alloy modify the crystal structure and effects the material austenite-martensite phase transformation.

The addition of Chromium has been known to increase hardness penetration. Its effects in steel are increase of toughness, as well as the wear resistence. Another characteristic, one of the most well known, is the tendency to resist staining and corrosion. Moreover, chromium increase critical temperatures in heat treatment. In additon to it, one of its disadvantages is its tendency to promote the growth of the austenite grain [8]. However, it is yet not known its effects in a CuAlNi shape memory alloy.

The present study aims to investigate the effect Cr presence has on Cu-Al-Ni microstructure, understand the thermochanical behavior and, through determination of phase transformation temperatures, analyze its influence in the alloy shape memory effect.

## 2. METHODOLOGY

The CuAlNiCr alloys were elaborated through plasma melting process, with vacuum control and argon gas injection. Each sample was processed two times to avoid billets and a heterogeneous microstructure. All the obtained samples were X-ray Fluorescence analyzed (see Table 1). It is possible to notice that the temperature of plasma melting process for a Copper based alloy causes a percentage of aluminum loss for alloy 2 and 3. Posteriorly, all the alloys underwent the same heat treatment of betatization, in order to obtain an ordered metastable β phase, being submitted to a temperature of 900°C for 15 minutes followed by water quenching at temperature of -1°C.

**Table 1** Nominal and analyzed chemical composition of alloys.

| Alloy Number | Nominal Chemical composition (wt.%) | | | | Analyzed Chemical composition (wt.%) | | | |
|---|---|---|---|---|---|---|---|---|
| | Cu | Al | Ni | Cr | Cu | Al | Ni | Cr |
| 1 | 80.36 | 13.72 | 3.92 | 2.00 | 80.57 | 14.15 | 4.54 | 0.74 |
| 2 | 79.54 | 13.58 | 3.88 | 3.00 | 82.98 | 11.04 | 4.54 | 1.44 |
| 3 | 78.72 | 13.44 | 3.84 | 4.00 | 82.2 | 10.8 | 4.61 | 2.26 |

After heat treatment, for microstructure characterization, all samples were polished and etched with Ferric Chloride for 35 seconds, and Scanning Eletron Microscopy (SEM) analized, following by X-ray Diffraction (XDR) from 30° to 100°. Thereafter, to detemine the endothermic and exotermic peaks, it was applied Differential Scanning Calorimetry (DSC) under dynamic nitrogen atmosphere from -80°C up to 200°C at a heating rate of 10°C/min.

## 3. RESULTS AND DISCUSSION

### 3.1. Scanning Electron Microcopy (SEM)

Fig. 2 shows SEM results for Sample 1 (a), 2 (b) and 3 (c), after heat treatment of betatization. All SEM have shown the presence of martensitic structure, typical of a structure that has undergone heat threament of betatization, with nanometrics needles.

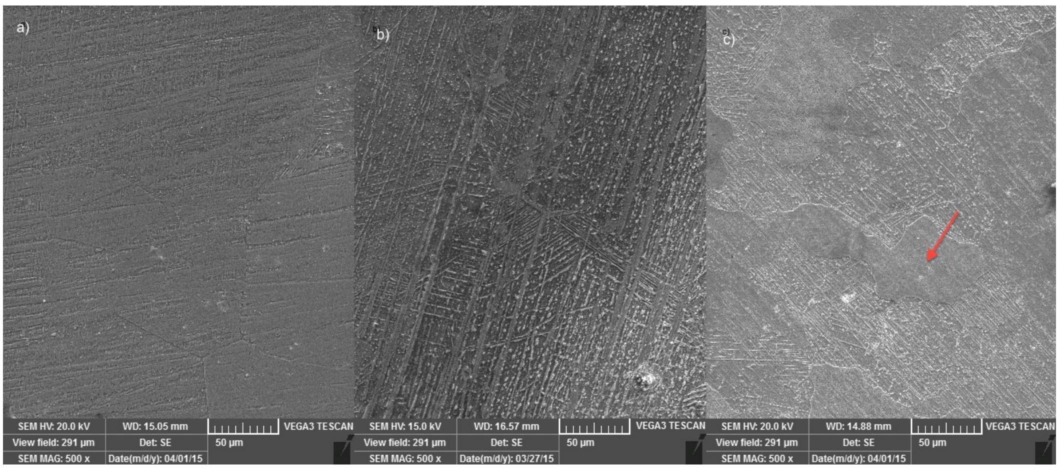


**Fig. 1** SEM of Samples 1, 2 and 3, respectively, after heat treatment of betatization.

Comparing Fig. 2a), Fig 2b) and Fig. 2c) it is notable that the samples contaning higher concentration of Cr have a more martensitic structure. Fig.2 c) shows the presence of austenite, directed by the red arrow, which proves that the higher the Cr percentages the higher the growth of austenite grain.

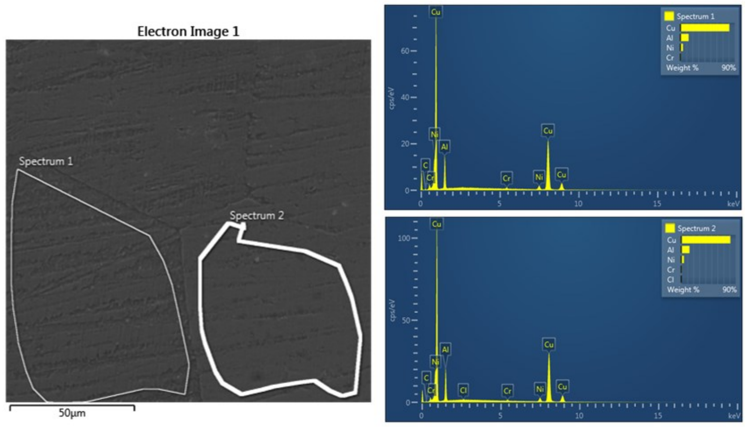


**Fig. 2** EDS Spectrum of Sample 1.

Further EDS and MEV investigations, it was also confirmed that the increase of Cr percentages results in a more martensitic structure. Looking at Fig. 3, the Spectrum 1 circled area presents a martensitic structure with a higher number of needles compared to Spectrum 2. EDS results, as showed at Table 2, proved that the presence of Chromium has a directly proporcional effect for development of martensite needles.

**Table 2** Analyzed chemical composition of alloy Sample 1 at the spectrum 1 and 2.

| Spectrum | Analyzed Chemical composition (wt.%) | | | |
|---|---|---|---|---|
| | Cu | Al | Ni | Cr |
| 1 | 81.08 | 13.71 | 4.43 | 0.78 |
| 2 | 81.14 | 13.62 | 4.45 | 0.63 |

### 3.2. X-ray Diffraction (XRD)

Fig. 3 shows XRD result of Samples 1 and 3, after heat treatment of betatization. The sample with less concentration of Cr presented a more homogeneous structure, showing predominantly $\beta'_1$, as displayed in Fig. 3 line “a“. However, the microstructure of Sample 3, line “b“ of Fig. 3, presented more than one phase, including martensitic phase $\beta'_1$ and austinitic phase. Concluding that Cr presence promotes the growth of austinitic phase.

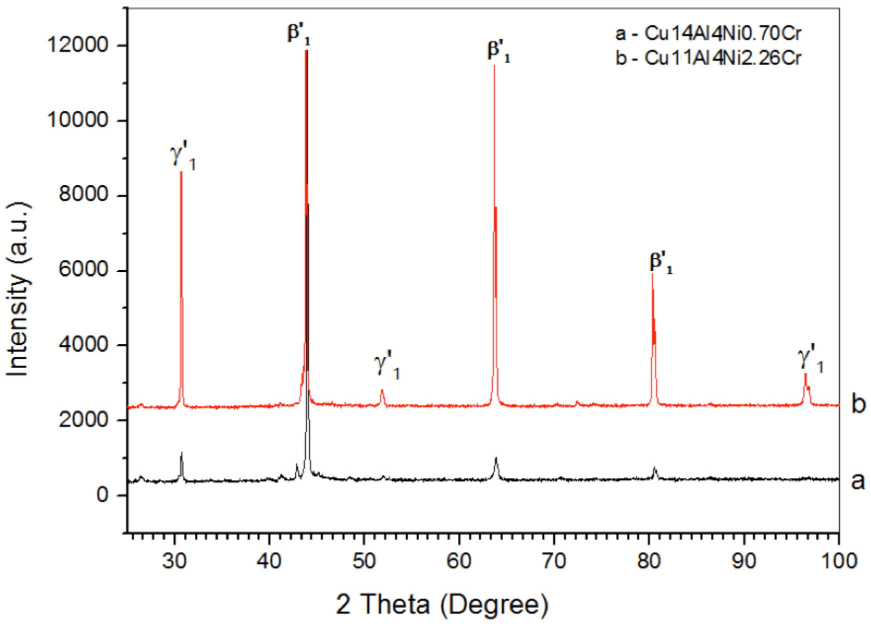


**Fig. 3** XDR result of Sample 1 (a) and Sample 3 (b).

### 3.3. Differential Scanning Calorimetry (DSC)

Fig. 4 and Fig. 5, show DSC result of sample 1, 2 and 3, after heat treatment of betatization.

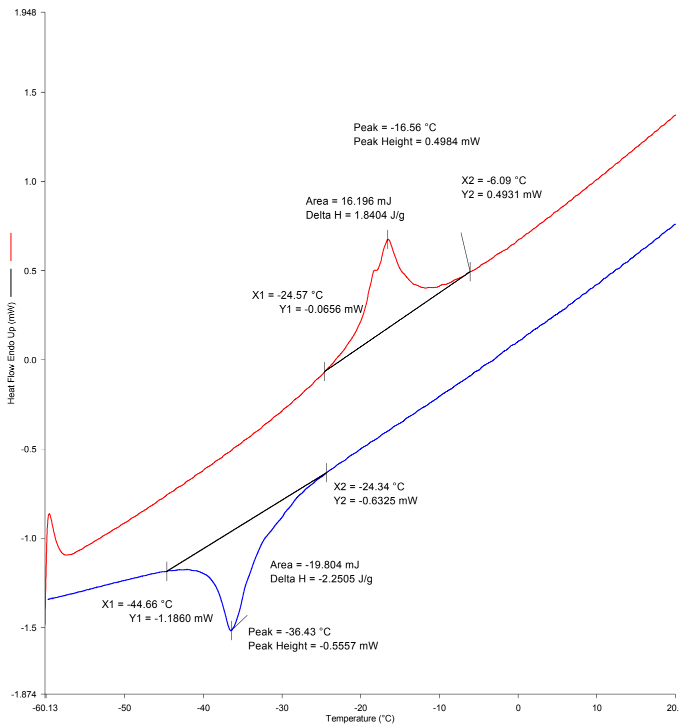


**Fig. 4 –** DSC result of Sample 1, 0.74% of Chromium in CuAlNi alloy.

Fig. 4 DSC result have shown that sample contaning 0.74% of Cr presents shape memory effect. Its temperatures of phase transformation are displayed at Table 3. Compared to Cu-Al-Ni previous researchs [9-11], there is a significant drop of phase transformation temperatures.

**Table 3** Temperatures of phase transformation Sample 1.

| Phase | Begin (°C) | End (°C) | Peak (°C) |
|---|---|---|---|
| Martensite | -44.66 | -24.34 | -36.43 |
| Austenite | -6.09 | -24.57 | -16.56 |

The DSC result of samples 2 and 3 have shown that amount of Cr higher than 1.44% causes the loss of memory shape effect, which can be explained by the X-ray diffration obtained for both samples, with presence of more than more phase.

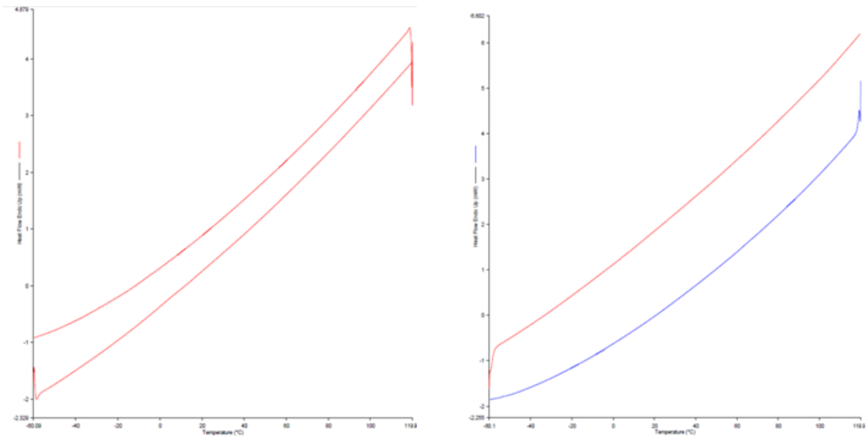

**Fig. 5** DSC result of Samples 2, to the left, and 3, to the right.

## CONCLUSION

The results have shown that the addition of Cr effects Cu-Al-Ni microstructure and its phase transformation temperature. The increase percentages of Cr has direct influence in its Memory Shape effect. For percenteges higher than 1.44%, the devoloped alloy does not present Memory Shape effect. However, to Sample 1 which has 0.74% of Cr presents memory shape. It is also notable that to the higher percenteges of Cr there is a increase of martensite structure and, presence of austenite grain for the sample containing 2.26% of Cr. For the phase transformation temperatures, the presence of Cr results in a decrease of both martensitic and austenitic transformation temperatures.

## ACKNOWLEDGEMENTS

***The authors would like to thank IFBA for the financial and structural support throughout the present paper development.***

## REFERENCES

[1] OTSUKA K., WAYMAN C. M. Shape Memory Materials. Cambridge University Press: Cambridge, 1998.

[2] AIZAWA, S., KAKIZAWA, T., HIGASINO, M. Case Studies of Smart Materials for Civil Structures. Smart Materials and Structures. v. 7, n. 5, 1998, pp. 617-626.

[3] SARI U., AKSOY I. Micro-structural analysis of self-accommodating martensites in Cu-11.92wt% Al-3.78wt% Ni shape memory alloy, Journal of materials processing technology 195, 2008, pp. 72–76.

[4] SARI U., KIRINDI T. Effects of deformation on microstructure and mechanical properties of a Cu-Al-Ni shape memory alloy. Materials Characterization 59, 2008, pp. 920-929.

[5] VAJPAI S. K., DUBE R. K., SANGAL S. Microstructural and properties of Cu-Al-Ni shape memory alloy strips prepared via hot densification rolling of argon atomized power preforms. Materials Science and Engineering A 529, 2011, pp. 378-387.

[6] VAJPAI S. K., DUBE R. K., SANGAL S. Application of rapid solidification powder metallurgy processing to prepare Cu-Al-Ni high temperature shape memory alloy strips with high strenghth and high ductility. Materials Science and Engineering A 570, 2013, pp. 32-42.

[7] LOJEN G., ANŽEL I., KNEISSL A. C., Microstruture of rapid solidified Cu-Al-Ni shape memory ribbons. 2005.

[8] SILVA A. L. V. C., MEI P. R. Aços e Ligas Especiais 2ª Editioin. Edgard Blücher: São Paulo, 2006.

[9] LIMA P. C. Obtenção e determinação da capacidade de amortecimento da liga Cu-14Al-4Ni pelo método de excitação por impulso. Brasília University: Brasília, 2013.

[10] GOJIĆ M., KOŽUH S., ANŽEL I., LOJEN G., IVANIĆ I., KOSEC B. Microstructural and Phase Analysis of CuAlNi Shape Memory Alloy after continuous casting. Materials and technology 47, 2013, pp. 149-152.

[11] KNEISSL A. C., UNTERWEGER E., BRUNCKO M., LOJEN G., MEHRABI K., SCHERNGELL H. Microstructure and properties of NiTi and CuAlNi Shape Memory Alloys. Metalurgija – Journal of Metallurgy, 2007, pp. 89-100.