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INFLUENCE OF CHROMIUM IN THE PHASE TRANSFORMATION TEMPERATURE OF A CUALNI SHAPE MEMORY ALLOY

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Abstract. *The thermomechanical recovery, inherent of Shape Memory Alloys (SMA), is directly related to martensitic transformation. Furthermore, the activation temperatures of martensite-austenite transformation depends of, among other factors, the alloy's grain size. In the present study, it was verified the influence that the addition of Chromium, in different percentages, in a Copper-Aluminum-Nickel SMA, has in the grain size. In addition, it was associated grain size with the beginning and ending temperatures of phase transformation. The CuAlNiCr alloy was obtained through plasma melting, equipment of the brand EDG model Discovery, which each sample was submitted four times to have a more homogeneous material. Posteriorly, it underwent heat treatment of betatization at temperature of 900°C. All of the obtained samples were sanded, polished and chemically attacked with Ferric Chloride. For the purpose of material characterization, it was applied Scanning Electron and Optical Microscopy, X-ray Diffraction (DRX) and Differential Scanning Calorimetry (DSC). As a result, with the addition of Chromium it is expected the refinement of the CuAlNi microstructure in order to have a better application.*

Keywords: *Phase Transformation Temperature, Grain Size, CuAlNi Alloy, Influence of Chromium*

1. INTRODUCTION

Shape Memory Alloy (SMA) have been an object of great interest in Engineering, due to its vast possible application field, such as: Medical (odontology and orthopedic), thermostat and motors (Otsuka and Wayman, 1998).

SMAs are considered smart materials for its unique memory shape effect (SME) and its superelasticity (pseudoelasticity). These remarkable properties are controlled by a reversible structural transformation, martensitic transformation (Balo and Sel, 2012). The phenomenon SME is noted when applied a deformation apparently plastic in a temperature below the start Austenite temperature (As), followed by heating above the finish Austenite temperature (Af) that causes crystallographic transformation, resulting in the alloys original shape return (Otsuka and Ren, 1999).

Among the various SMAs, the CuNiAl stands out economically for a relatively lower cost (Cândido, 2010). Nevertheless, CuAlNi have some limitations, such as brittleness, due to large grain size, which has been a major prohibitive factor in their commercial utilization (Sari and Kirindi, 2008;Vajpai, et. al., 2011). Aiming a better applicability, by grain refinement, it is common to add a quaternary element (Vajpai, et. al., 2011; Vajpai, et. al., 2013). Previous researches have studied the addition of Boron and Chromium to CuAlNi alloy to obtain better mechanical properties (Loejn, et. al., 2005; Teixeira, et. al., 2015). Thereby, the addition of a material strange to the alloy modifies the crystal structure and effects the material austenite-martensite phase transformation.

The present study aims to verify the influence addition of Cr has, associating grain size, in the microstructure and mechanical properties of CuAlNi SMA, characterizing the specimens using Scanning Electron and Optical Microscopy, X-ray Diffraction and Differential Scanning Calorimetry.

2. METHODOLOGY

In a plasma melting furnace, with vacuum control and argon gas injection, different percentages of Cr (2, 3 and 4 wt%) were added to a Cu14Al4Ni alloy. In order to avoid billets and a heterogeneous microstructure, all specimens were processed two times during 23s each. X-ray Fluorescence was applied to obtain the chemical composition. Posteriorly, to obtain an ordered metastable β phase, all samples underwent the same heat treatment of betatization, in tube furnace at a temperature of 900°C for 15 minutes followed by water quenching at temperature of -1°C.

Subsequently, to characterize their microstructure, all specimens were polished and etched with Ferric Chloride for 35s, and Scanning Eletron Microscopy (SEM) and Optical Microscopy analyzed, followed by X-ray Diffraction (XDR) from 30° to 100°. Thereafter, it was applied Differential Scanning Calorimetry (DSC), under dynamic nitrogen atmosphere from -60°C up to 120°C at a heating rate of 10°C/min, to determine the austenitic start temperature (A_S), austenitic finish temperature (A_f), martensitic start temperature (M_S) and martensitic finish temperature (M_f).

3. RESULTS AND DISCUSSION

3.1 X-ray Fluorescence

The X-ray Fluorescence result is shown in Tab. 1. The plasma melting process temperature for a Copper based alloy caused loss of aluminum percentage for alloys B and C. In addition, it is notable the Cr percentage loss due to the obtaining plasma melting process as Cr was added in compressed form.

Table 1. X-Ray Fluorescence result for samples A, B and C.

Alloy	Analyzed Chemical composition (wt.%)			
	Cu	Al	Ni	Cr
A	80.57	14.15	4.54	0.74
B	82.98	11.04	4.54	1.44
C	82.2	10.8	4.61	2.26

3.2 Scanning Electron Microscopy and Optical Microscopy

Figure 1 show SEM results for sample A, B and C, after heat treatment of betatization. As a typical microstructure that has undergone heat treatment, all SEM have shown the presence of martensitic structure with nanometrics needles. The microscopy verified the presence of austenite grain for sample C as well.

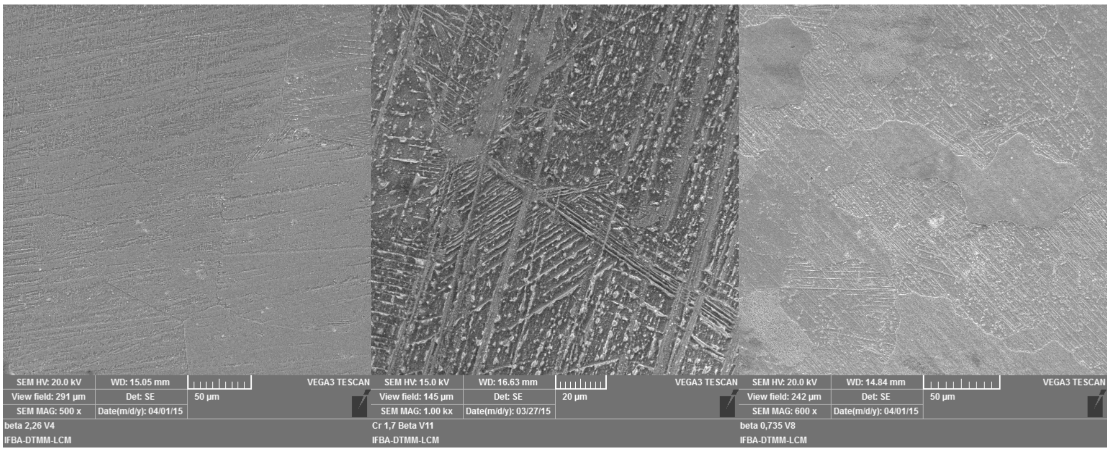


Figure 1. SEM results for sample A (left), B (middle) and C (right) (Ferric Chloride).

For the purpose of comparison, it was elaborated a CuAlNi SMA that underwent the same manufacturing process and heat treatment. The Optical Microscopy, taken with same zoom, 80x, for all pictures, has shown that the addition of Cr has a great grain size impact. Figure 2 shows CuAlNi SMA microstructure, as expected with a large grain size.

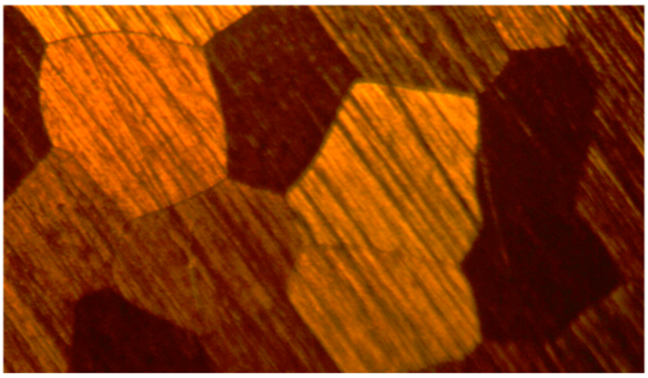
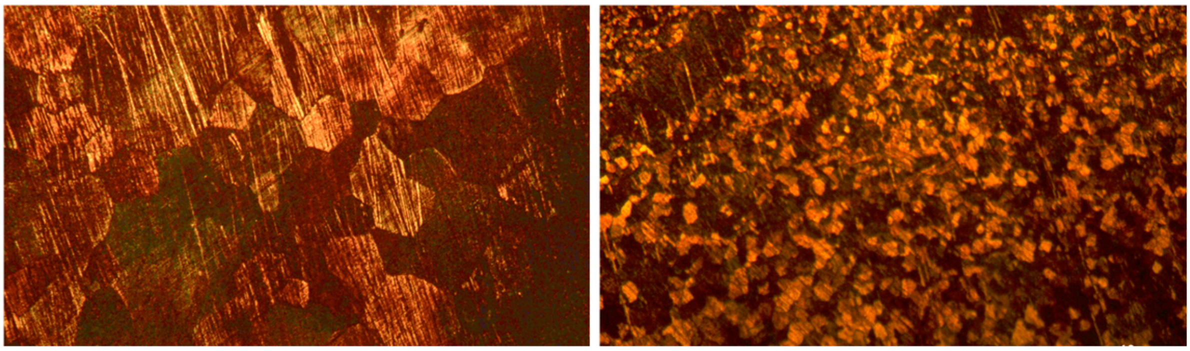


Figure 2. Optical Microscopy result of a CuAlNi SMA, zoom of 80x (Ferric Chloride).

However, when compared to Fig. 3, displaying the microstructure of sample A and C, there is a considerable grain size reduction. Noting that a higher percentage of Cr results in smaller grains.



(a) (b)

Figure 3. Optical Microscopy of samples A (a) and C (b), both zoom of 80x (Ferric Chloride).

3.3 X-ray Diffraction

XRD results have confirmed that the increase of Cr amount affect austenite grain development. As shown in Fig. 4 line “a”, the sample with less concentration of Cr, sample A, presented a more homogeneous structure, mainly martensitic phase β‘$_1$. Meanwhile, sample C, shown at Fig. 4 line "b", presented a microstructure with more than one phase, including martensitic phase β‘$_1$ and austenite phase. Concluding that Cr presence promotes the growth of austenitic phase.

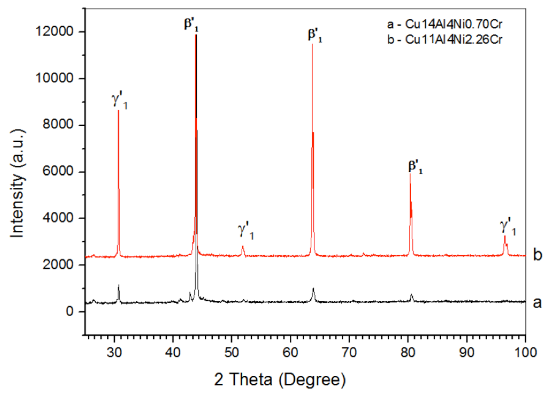


Figure 4. XRD result of sample A (line "a") and sample C (line "b")

3.4 Differencial Scanning Calorimetry

DSC results have confirmed that Cr affect SME of the analyzed alloys. Figure 5 and Fig. 6 shows DSC result of sample A, B and C after heat treatment of betatization.

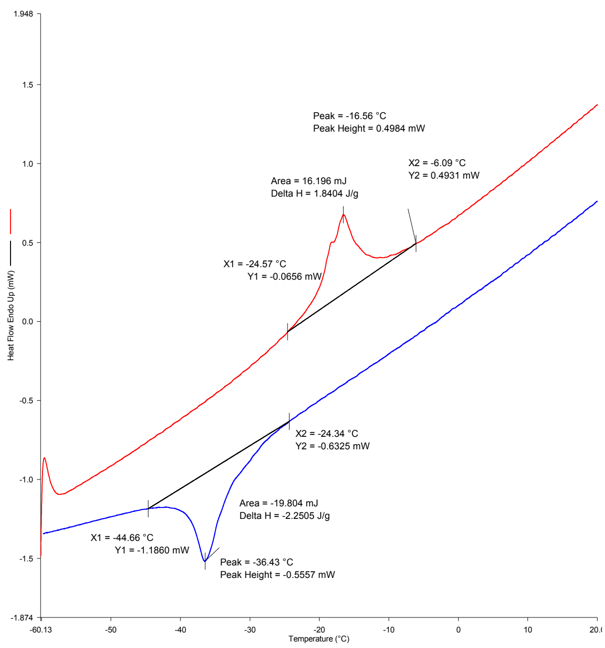


Figure 5. DSC result of sample A.

DSC result has shown that, for sample A containing 0.74% of Cr, present shape memory effect as seen in Fig. 5. Its temperatures of phase transformation are displayed at Table 2. Compared to Cu-Al-Ni of recent works (Lima, 2013; Gojić, et. al., 2013; Kneissl, et. al., 2007), there is a significant drop of phase transformation temperatures.

Table 2. Sample A temperature of phase transformation.

Phase	M_s	M_f	A_s	A_f
Temperature (°C)	-44.66	-24.34	-6.09	-24.57
Peak (°C)	-36.43		-16.56	

Figure 6 displays DSC result of samples B and C. The presence of Cr higher than 1.44% causes the loss of memory shape effect, which can be explained by the X-ray diffraction obtained for both samples, with presence of more than more phase.

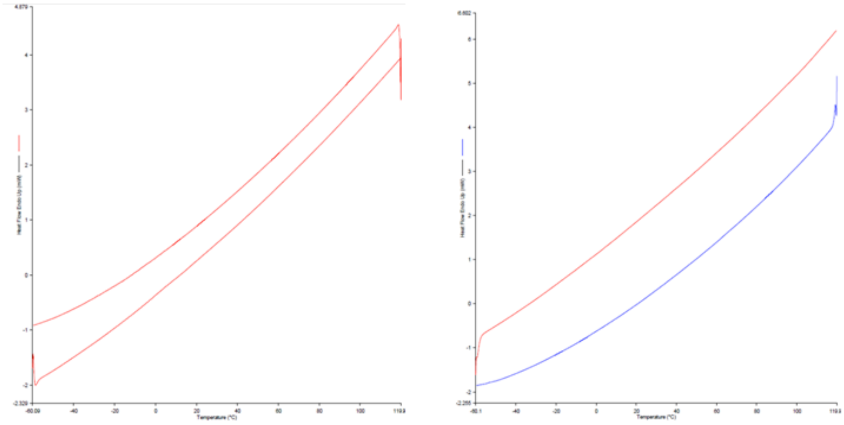


Figure 6. DSC result of sample B (left) and sample C (right).

4. CONCLUSION

The addition of Cr affects CuAlNi microstructure and its phase transformation temperature. Results have shown that the increase of Cr percentage has direct influence in its SME and the alloys grain size. For percentages higher than 1.44%, the developed alloy does not present SME and it was detected austenite grain presence for the specimen containing 2.26%. However, for Sample A which has 0.74% of Cr presents memory shape. The grain size showed a substantial reduce when added Cr to the microstructure. As smaller the grain, as seen for sample A, there was a decrease of both martensitic and austenitic transformation temperatures comparing to previous works.

5. ACKNOWLEDGEMENTS

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