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Influence of the Deep Cryogenic Treatment at the Stabilization of Martensitic Transformation Temperatures at the Smart Material Alloy Cu-14Al-4Ni

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Abstract: DCT (deep cryogenic treatment) is commonly used in industry to improve the wear resistance characteristics of steels, especially. However, there are just a few researches about the effects on non-ferrous metals. The purpose of this work was to investigate how DCT affects the properties of Cu-14Al-4Ni alloy treated at different soak time and submitted to thermomechanical cycling. A comparative experimental analysis was performed of the thermal properties of alloys obtained on a vacuum furnace, treated by DCT and thermomechanically cyclized. The results indicates that thermomechanical cycling promoted the appearance and growth of the martensitic phase γ'_1, less ductile than the martensitic phase β'_1, which together with the induced hardening produced an increase in transformation temperatures and microhardness. The higher the number of cycles, the greater these effects. The DCT promoted an increase in the intensity of the diffraction peaks corresponding to the phase β'_1 and the maintenance of them during the thermomechanical cycling of the material, which indicates that the DCT stabilizes the martensitic phase β'_1 and, consequently, caused a reduction and stabilization of the martensitic transformation temperatures and the microhardness, when compared to the untreated material. The longer the soaking time of DCT, the greater these effects.

Key words: DCT, SMA (shape memory alloy), Cu-Al-Ni alloy.

Nomenclature

DCT	deep cryogenic treatment
SMA	shape memory alloy
EDS	energy dispersive spectroscopy
XRD	X-ray diffraction
$T\,M_{peak}$	peak temperature of martensitic transformation
$T\,A_{peak}$	peak temperature of austenitic transformation

Greek Letters

β'_1	martensitic phase
γ'_1	martensitic phase
β_1	high temperature phase
2θ	diffraction angle

1. Introduction

The study of shape memory alloys (SMAs) has been explored in recent decades, due to their properties, such as mechanical work due to the shape change of the material when exposed to different temperatures [1]. SMAs are a group of metallic materials with the property to recover the original shape (shape memory effect) by imposing higher temperatures, due to inducing phase transformations in the material and thermoelastic properties of pseudoelasticity [2, 3].

Cu-Al-Ni system alloys have good thermomechanical properties, good shape recovery and higher hysteresis. Another factor that justifies the use of this type of system is its low cost of material acquisition and certain facilities observed at the alloy's manufacturing, reducing the cost of production in relation to Ni-Ti based systems [4, 5].

One of the factors that reduce the application of Cu-Al-Ni alloys is the reduction of the stabilization capacity of the martensitic/austenitic phases.

Different processes for the elaboration of SMA have been studied along the techniques of thermomechanical treatment and addition of refining elements in order to reduce the level of complexity of the austenite/martensite transformation, like the DCT (deep cryogenic treatment) [6-8].

DCT is treatment that consists of using temperatures closer to liquid nitrogen temperature (-196°C) and subsequent stabilization at room temperature, in order to obtain certain properties, such as high wear resistance, toughness, hardness and compressive residual stress, among others, and the use of this process is increasing [9]. However, further

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research is required in relation to the different soaking time and the alterations obtained into the SMA and those related to the CuAlNi system, associated with the most appropriate method of elaboration. Thus, not only would the low cost must be a selection criteria, but also the improved properties could be better explored, with emphasis to the capacity of inhibiting the loss of shape recovery capacity, which is directly associated to the stabilization of martensite phase.

2. Experimental Setup

The alloy was vacuum melted in an induction furnace of 24 kVA, using a crucible of silicon carbide. The melted alloy was chill-cast and, after solidification, it was water-cooled at 25°C. After casting, the ingot was homogenized at 950°C, during 15 min. Then, the alloy was submitted to an analysis of X-ray fluorescence to verify the chemical composition. Then, the ingot was hot-rolled (2%, approximately), in order to standardize the thickness.

The ingots were sectioned by electroerosion in 36 wires with 1 × 0.8 × 6 mm dimensions. Different samples were cooled at -196°C at rates of 20°C/h on cooling and heating, and kept at this temperature for 2h, 12h and 24h.

The wires (samples) were embed in one side and were submitted to thermomechanical cycling, performed with a plier and a 1° precision graded gauge, to standardize the process, executing 100, 250 and 500 cycles. During the cycling, the samples were submitted to temperatures higher than 120°C to be sure that the initial shape was recovered.

After treatment and cycling, the samples were analyzed by XRD (X-ray diffraction), X-ray fluorescence, differential scanning calorimetry, confocal laser microscopy, scanning electron microscopy, Vickers microhardness and grain size measurement.

3. Experimental Results

In order to determine the chemical composition and to verify the uniformity of the microstructure of the produced ingot, X-ray fluorescence analysis and EDS (chemical dispersion energy analysis) were performed.

The EDS microanalysis, performed at several points per region suggests uniformity of the chemical composition of the melted alloy. Variations on chemical composition induce changes in martensitic transformation temperatures, and this control is mandatory. The EDS microanalysis results can be seen in Table 1.

Table 1 Chemical composition of the Cu-14Al-4Ni.

Element	Concentration (weight %)
Cu	82.3
Al	14.0
Ni	3.7

The results of diffractometric analysis of Cu-14Al-4Ni alloy presented three phases: martensitic $\gamma'_1$and β'_1, and $AlCu_3$ type, respectively, and high temperature phase β_1. This result can be seen in the Fig. 1.

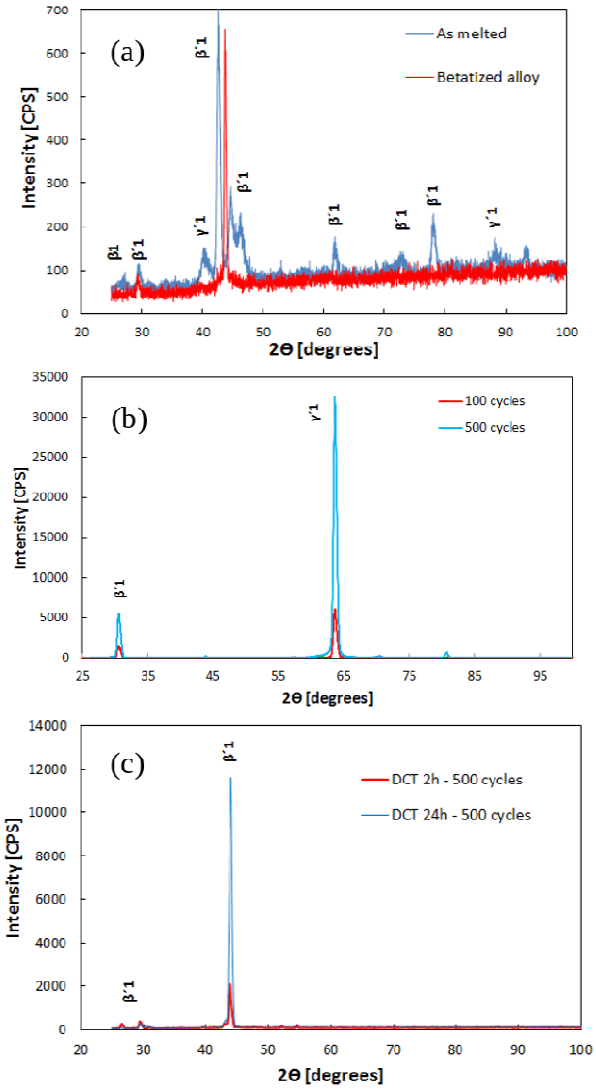

Fig. 1 Results of the XRD analyses of: (a) as melted and betatized samples; (b) samples without DCT after 100 and 500 cycles; (c) samples with DCT time of 2h and 24 h after 500 cycles.

Thermomechanical cycling induced the decrease of the martensitic phase β'_1, which appears at 43°, and the appearance (increase of intensity) of the γ'_1 phase

(also martensitic). Since it is less ductile than the β'_1 phase, it causes the gradual loss of the memory effect, observed through the rise of the transformation temperatures, microhardness and loss of shape recoverability.

After the greater amount of cycling, the γ'_1 phase showed the higher intensity at 65°. This is the phasewhich provokes the loss of shape recovery. DCT stabilized the β'_1 martensitic phase at 43°, suppressing the γ'_1 phase.

The samples were submitted to DSC thermal analysis in steps of 40°C/min in a temperature range between 0°C and 120°C. Subsequently, they were submitted to differential thermal analysis using a heating/cooling rate of 15°C/min in the same temperature range. Through the test it was possible toverify the phase transformation temperatures, the transformation enthalpies and the hysteresis level of each sample. These results are shown in Figs. 2 and 3.

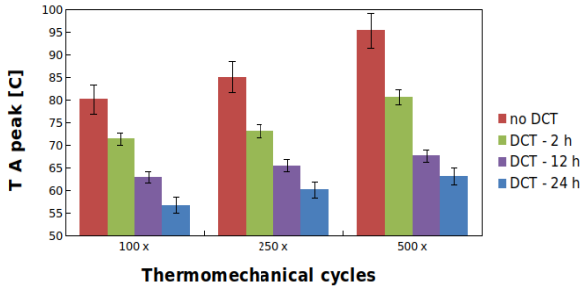

Fig. 2 Comparative graph of peak austenitic transformation temperatures for samples cycled with and without DCT.

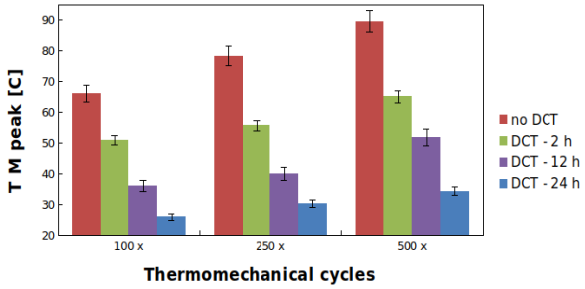

Fig. 3 Comparative graph of peak martensitic transformation temperatures for samples cycled with and without DCT.

The transformation temperatures, both in the forward and reverse direction, increase as the number of thermomechanical cycles increases, thus a greater input of energy is required to produce the shape memory effect. DCT caused a reduction in material transformation temperatures. In addition, the longer the DCT soaking time, the lower the transformation temperatures. This behavioral change caused by DCT may be related to the higher occurrence (higher intensity presented in XRD with increasing DCT time) of the ordered phase β'_1 (the phase stronger, responsible for the shape memory effect).

The hysteresis (difference between martensitic and austenitic peak temperatures) increases as DCT soaking time increases, with values greater thandouble under some conditions, compared to untreated material (Table 2).

Since hysteresis in SMAs is directly related to internal damping and this to various phenomena in microstructural defects, such as grain boundaries, impurities and disagreements, cryogenic treatment may have somehow acted on these defects in such a way, causing this increase in material hysteresis.

Table 2 Peak transformation temperatures.

Samples	$T\,M_{peak}$ (°C)	$T\,A_{peak}$ (°C)	Hysteresis (°C)
no DCT 100×	66.12	80.21	14.09
no DCT 250×	78.25	85.12	6.87
no DCT 500×	89.53	95.34	5.81
DCT 2h 100×	51.02	71.42	20.40
DCT 2h 250×	55.73	73.12	17.39
DCT 2h 500×	65.16	80.62	15.46
DCT 12h 100×	36.09	62.87	26.78
DCT 12h 250×	40.05	65.53	25.48
DCT 12h 500×	45.87	67.72	21.85
DCT 24h 100×	26.05	56.82	30.77
DCT 24h 250×	30.26	60.22	29.96
DCT 24h 500×	34.42	63.10	28.68

The significant decrease in hysteresis as the number of cycles increases may be related to the reorientation of martensite variants, caused by successive material deformations and heating.

Microscopic analysis was performed in confocal laser microscopy in the cross section of the lamination, where the wires were sectioned by electroerosion, showing, in all samples, martensitic matrix (β'_1 phase), with grains showing well defined contours with polygonal morphology, with equiaxial tendency, with needle aspects, without pores or inclusions.

From the presented microscopy results (Figs. 4 and 5), it is not possible to observe morphological or microstructural changes in the samples due to the thermomechanical cycling performed. However, regarding the sample submitted to DCT, it is possible to observe a noticeable increase in the thickness of the martensite needles as the DCT soaking time increased. This fact may be related to the increase in the intensity of the peaks corresponding to the β'_1 phase presented in the XRD results.

It was not possible to observe morphological or

microstructural changes in the samples due to the thermomechanical cycling performed.

The grain size measurements show the DCT, regardless of the soaking time, did not produce significant changes in the grain's size (between 200 and 230 μm), keeping the same behavior related to cycling whencompared to alloy without DCT.

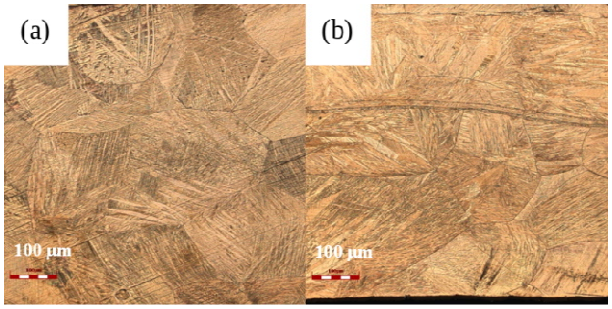

Fig. 4 Confocal micrography of the Cu-14Al-4Ni alloy, without DCT, with (a) 100 cycles and (b) 500 cycles.

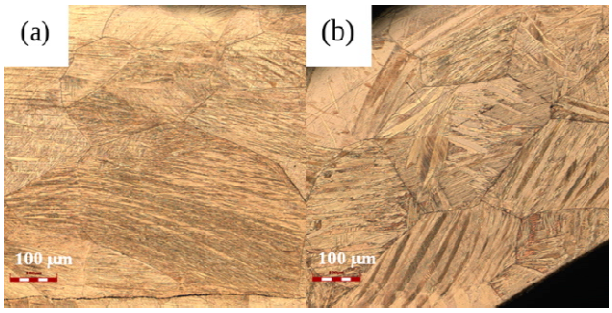

Fig. 5 Confocal micrograph of the Cu-14Al-4Ni alloy, with 24h DCT, with (a) 100 cycles and (b) 500 cycles.

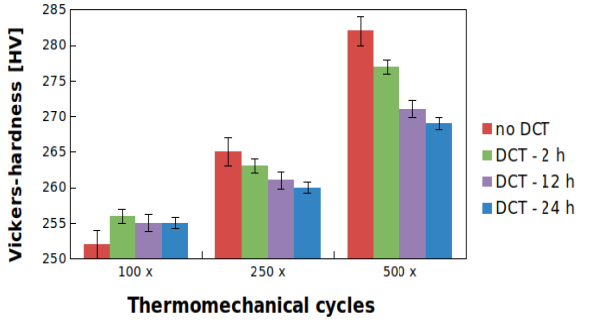

Fig. 6 Vickers micro hardness test results of the thermomechanically cycled samples with and without DCT.

For the Vickers microhardness, means and standard deviations of 15 indentations in 3 distinct regions of each sample were calculated. Analyzing the Vickers microhardness results and considering the standard deviation (Fig. 6), the microhardness presents a small increase with the increase of the number of cycles. For samples submitted to DCT, this increase in microhardness values with increasing number of cycles is minimized (the rate of microhardness increasing according to the number of cycles is smaller).

In addition, the longer the DCT soaking time, the smaller the microhardness of the material increases with increasing number of cycles. This behavioral change due to DCT must be related to the stabilization of the more ductile martensitic phase β'_1 which is responsible for the shape memory effect [10].

4. Conclusions

This work investigated the microstructural and thermomechanical changes at the Cu-14Al-4Ni alloy submitted to DCT, at different soak time, and thermomechanically cycled in different cycles. The main conclusions are:

(1) Based on the diffraction analysis, the used manufacturing process suppressed the precipitation of the α-phase, high copper hardness intermetallic phase, and produced an orthorhombic martensitic microstructure of $AlCu_3$ (β'_1) type, typical of SMA.

(2) DCT induced the increase in the intensity of the diffraction peaks (increase of the volumetric fraction) corresponding to the phase (β'_1) and, consequently, the maintenance of these during the thermomechanical cycling of the material, indicating that the DCT stabilized the ordered orthorhombic martensitic phase (β'_1).

(3) DCT produced a sensitive stabilization of the microhardness of the material submitted to thermomechanical cycling. This behavior may be related to the stabilization of the orthorhombic orderly phase of the $AlCu_3$ type (β'_1), more ductile than the martensitic phase (γ'_1) and responsible for the alloy's shape memory effect. The longer the soaking time of DCT, the greater these effects.

(4) Related to the hysteresis, the higher the soaking time of the DCT, for the thermomechanically cycled samples, the greater the difference between the peak temperatures of the direct and reverse martensitic transformation. This behavior is directly related to the internal damping of the material (friction between the martensite plates) and this, to several phenomena in microstructural defects, in such a way that the cryogenic treatment may have acted in some way in these defects in order to cause this increase in the hysteresis of the material.

(5) DCT did not produce significant changes in grain sizes.

Acknowledgments

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