MICROSTRUCTURAL EVOLUTION STUDY OF Cu-14Al-4Ni SHAPE MEMORY ALLOY

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Abstract. *The non-ferrous shape memory alloys have, normally, two problems that hinder its use in industrial scale: the natural aging and grains growth. The first degrades the memory effect, while the second, observed during the processing of alloy, modifies the temperatures which the transformations occur. Therefore, the objective of this study is to determine the activation energy of the grain growth process of Cu-14Al-4Ni shape memory alloy, in order to promote the stabilization of the alloy delaying its aging. The alloy was melted in an induction furnace of 24 kVA. After casting, the bulk samples of the alloy were homogenized for 24 hours, solubilized and hot rolled followed by water-quenching to initiate the recrystallization. Then, samples of alloy were treated with isothermal aging for two hours at different temperatures in order to establish a law for the grain growth. Following the heat treatments, all annealed samples were examined by statistical metallography and the grain sizes were measured. After measurements, the ln [D-Do] x 1/T diagrams were plotted to determine the activation energy of the process from the empirical law of grain growth. The results showed that the alloy Cu-14Al-4Ni is extremely sensitive to temperature variation in which the alloy is treated, having a dual kinetics of grain growth. In the first domain, between 670 and 710 °C, the diagram provides a value for the activation energy equal to 39.32 KJ/mol, in the second domain, between 710 and 790 °C, the diagram provides a value for the activation energy equal to 9.01 KJ/mol.*

Keywords*: Shape Memory Alloys, Microstructure Evolution of CuAlNi, Grain Growth in a CuAlNi SMA*

1. INTRODUCTION

The shape memory effect (SME) can be defined as the capacity of a material, after being plastically deformed in its martensitic state, back to original shape by heating at temperatures above the martensitic transformation temperature. This occurs through a transformation of its crystalline structure of martensite to austenite via thermal processes, resulting in large deformations. The interesting thing about these materials, which is in its reconstitution to the original shape, the shape memory alloys can realize mechanical work. A wire can, for example, be tensioned from its memorized form; its length decreases under heating can be used in this case as actuator in robotic or biomechanics applications. In this case, the actuator behaves similarly to a muscle, sometimes incurring now relaxing. The achievement the SME is due to heat treatment to which the alloy is submitted. The alloys of the CuAlNi system with shape memory effect present two problems that hinder their employment on an industrial scale: these are the natural ageing and the grain growth observed during thermomechanical processing. The first degrades the shape memory effect, while the second, observed during thermomechanical processing of the alloy, displaces the temperatures where the thermoelastic transformations are observed. The extent of the ageing and grain growth can be reduced by control of the rate of atomic diffusion of the solute elements from the matrix to the grain boundaries.

At present three major groups of SMA have been studied: the NiTi alloys (NiTi, NiTiNb and NiTiFe) (Silva, 1998, 1999 and 2005), copper alloys (CuZn, CuAl, CuZnAl and CuAlNi) (Ferreira, 1998; Lima, 2000 and Gonzalez, 2007) and ferrous alloys (system FeMnSi) (Otsuka and Wayman, 1998). Besides these systems, several others have been developed and studied by universities and research centers around the world. Due to its thermomechanical properties of activity, the SMA are finding increasing applications in many areas (marine, aviation, nuclear, automotive, home appliances, robotics, medical and odontological, among others) (Duerig et al, 1990; Furuya and Shimada, 1990; Van Humbeeck, 1999; Schetky and Wu, 2000).

This paper has for objective the study of microstructural evolution of non-ferrous alloys with shape memory effect, in particular the Cu-14Al-4Ni, in order to promote the stabilization of the alloy delaying its aging. This study will allow the future realization of research projects aiming to develop devices for vibration control and shape control, such as a vibration isolator and a pseudoelastic bearing adaptive.

2. EXPERIMENTAL METHODS

Firstly, were determined the treatment temperatures (homogenization, solubilization and aging) by analyzing the phase diagram for the CuNiAl system alloys (Fig. 1 and 2). The alloy was melted in a RF furnace of 24 kVA, using a crucible of silicon carbide. The casting was made in air, without a protective atmosphere. The melted alloy was chill-cast and, after solidification, it was water-cooled at 25 °C, approximately. After casting, ingot with 15 x 30 mm section, approximately, was homogenized at 750 °C, during 24h. 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. After homogenization, the alloy was solution treated at 900°C for one hours. At this temperature, the ingot was hot-rolled 5% by steps up to 20% of deformation. Following hot rolling, the ingot was water-cooled to avoid total recrystallization. The ingot, partially recrystallized, was cut in small blocks and were annealed for two hours at different temperatures (670, 710, 750 and 790 °C) to achieve grain growth. For thermomechanical treatments samples were heated in a muffle furnace, monitored by a chromel-alumel thermocouple (accuracy ± 3 °C). The deformations were made in a goldsmiths rolling mill. For thermal treatment the same muffle furnace was used. After heat treatment, specimens were prepared by conventional metallographic techniques. The microstructures of these specimens, heat-treated at different temperatures, were observed by optical microscope for the statistical measurements of the grain size using a *"Quantikov"* digital analysis method. To describe the kinetics of the grain growth the same empirical relation (*Arrhenius)* was found to apply for the alloy, given by Eq. (1).

$$D^2 = D_0^2 + k_0.t.exp[-E_A/RT] \quad (1)$$

Where *(D)* is the diameter of the grain, (D_o) is the initial diameter, *(t)* is the time of treatment, (k_0) is the frequency factor, (E_A) is the activation energy of the process, *(R)* is the gas constant and *(T)* is the absolute temperature.

Finally, the $ln\ [D-D_o]\ x\ 1/T$ diagrams were plotted in order to establish the kinetic behavior and, based on these diagrams, the activation energies for grain growth were estimated for the Cu-14Al-4Ni alloy.

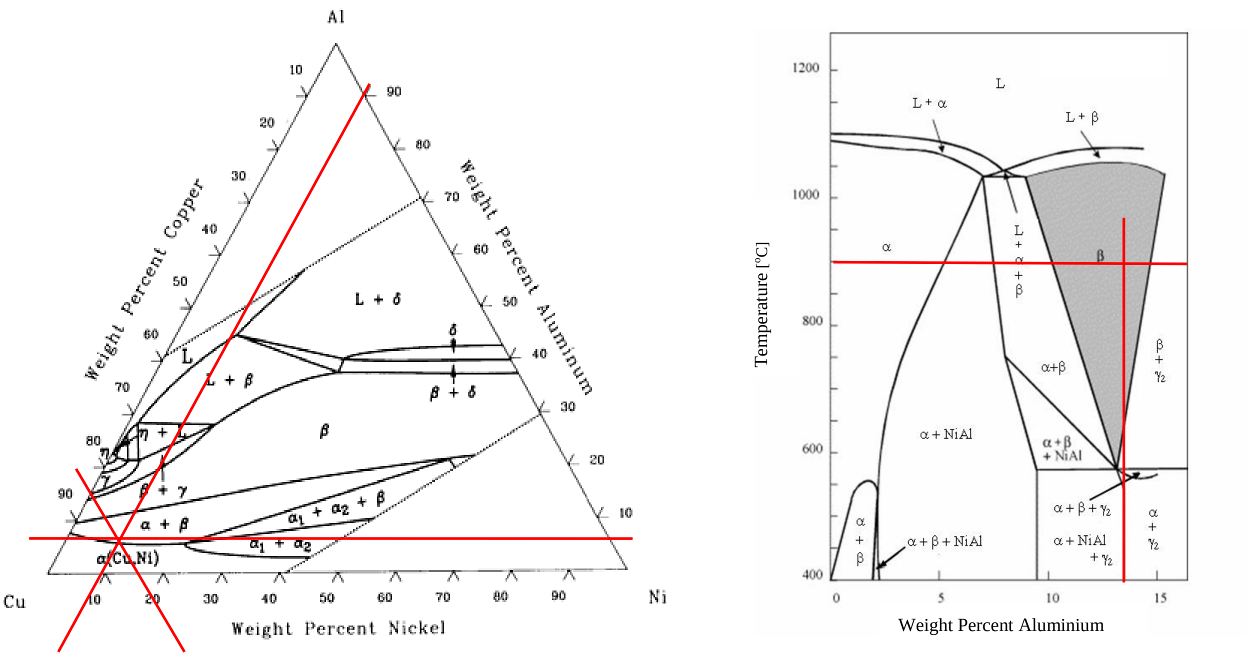

Figure 1. Phase diagram for CuAlNi and CuAl system alloys on an isothermal section at 900 °C (Köster, 1948).

3. RESULTS AND DISCUSSION

The chemical composition of the alloy studied is shown in Tab. 1.

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

Element	Concentration [weight %]
Cu	82,17
Al	13,87
Ni	3,96

The alloy obtained in as-casting condition (Fig. 2) presented a good workability and a relatively uniform morphology, although the material showed a very heterogeneous microstructure due to the melting and casting process (irregular solidification). It can be observed in Fig. 2 the presence of two characteristic phases of as-casting state: phase α, in the form of dendrites of FCC-type crystalline structure, and the phase clearer β (matrix), of BCC-type crystalline structure.

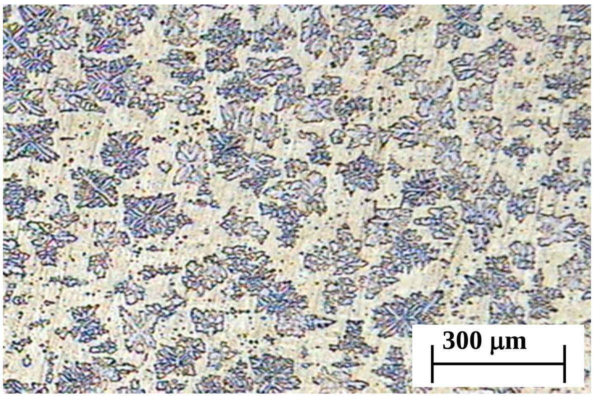

Figure 2. Optical microscopy micrographs of Cu-14Al-4Ni alloy in as-casting state (biphasic structure). Attack with ferric perchlorate solution at 5%.

After treatment of homogenization at 750 ºC for 24 hours, the material began to show a still biphasic structure, but without dendritic structure, with the presence of precipitates of the dispersed phase γ_2 in addition to the phase β (matrix) and phase α at grain boundary (Fig. 3).

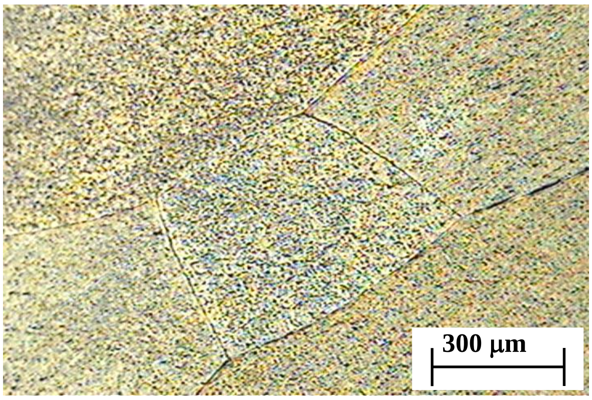

Figure 3. Optical microscopy micrographs of Cu-14Al-4Ni alloy homogenized at 750ºC for 24 hours. Attack with ferric perchlorate solution at 5%.

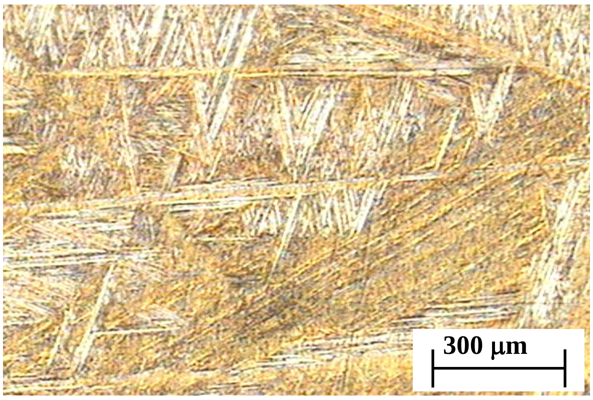

Figure 4. Optical microscopy micrographs of Cu-14Al-4Ni alloy solubilized at 900ºC for 1 hour and hot rolled with subsequent cooling in water. Attack with ferric perchlorate solution at 5%.

The material annealed at 900 °C for 1 hour and hot rolled (δ = 20%) at this temperature with subsequent cooling in water presented a uniform microstructure of monophasic martensitic structure in the form of needles (variant monoclinic β'), as shown in Fig. 4. By presenting an excellent workability, this metastable phase (β') allowed the material to support a deformation of 20% without causing cracks or breaks in the sample. The average grain size found for these samples was 2.866 ± 0.327 mm.

The Figures 5, 6, 7 and 8 show the microstructures of samples of the Cu-14Al-4Ni alloy submitted to aging treatment for 2 hours at 670, 710, 750 and 790 °C, respectively.

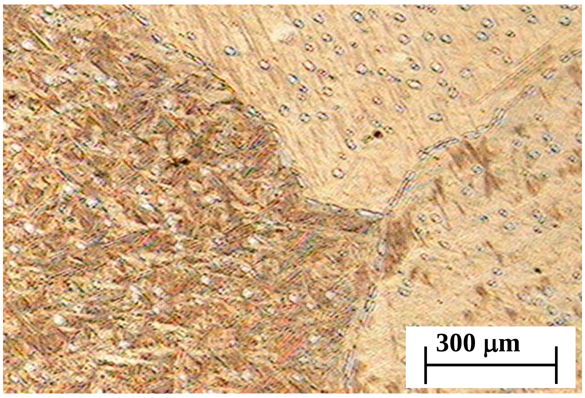

Figure 5. Optical microscopy micrographs of Cu-14Al-4Ni alloy submitted to aging treatment at 670 °C for 2 hours with subsequent cooling in water. Attack with ferric perchlorate solution at 5%.

It can be observed in Fig. 5 the presence of a biphasic structure with precipitates (phase α) in the region of grain boundary (preferentially) and dispersed through the matrix of β phase. It is possible see also an appreciable increase in grain size when compared with previous samples. This result suggests that there was a slight escape of nominal composition of the material, moving the domain of β phase to the right, thus requiring a higher temperature treatment. This behavior can be explained by the high heterogeneity of the material caused by solidification in metal ingot mold (ingot regions with different chemical composition). The average grain size found for the samples aged at 670 °C was 3.069 ± 1.220 mm.

The samples treated at 710 ºC, differently those treated at 670 ºC showed a microstructure martensitic uniform, predominantly phase β' (needle-shaped), but with some amount of orthorhombic phase $\gamma`_2$ (acicular), as shown in Fig. 6. Such behavior can also be justified by compositional heterogeneity of the alloy (ingot). The average grain size found for the samples aged at 710 °C was 3.842 ± 0.821 mm.

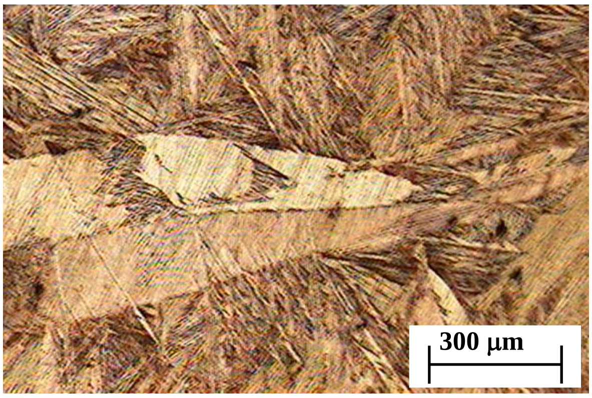

Figure 6. Optical microscopy micrographs of Cu-14Al-4Ni alloy submitted to aging treatment at 710 °C for 2 hours with subsequent cooling in water. Attack with ferric perchlorate solution at 5%.

With respect to samples treated at 750 and 790ºC (Figs. 7 and 8), both showed a more uniform microstructure as well as the previous, practically formed by martensitic phase with monoclinic structure of β' type (needle-shaped). It is also possible observe a sensitive increase in grain size, especially for the sample treated at 790ºC (Fig. 8). The average grain sizes were found for the samples aged at 750 and 790 °C were 4.128 ± 0.615 and 4.675 ± 1.065 mm, respectively.

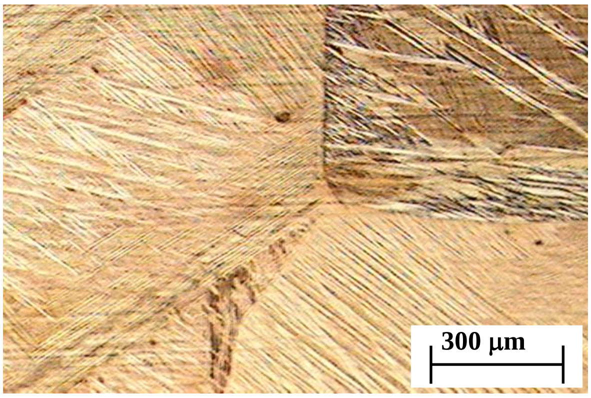

Figure 7. Optical microscopy micrographs of Cu-14Al-4Ni alloy submitted to aging treatment at 750 °C for 2 hours with subsequent cooling in water. Attack with ferric perchlorate solution at 5%.

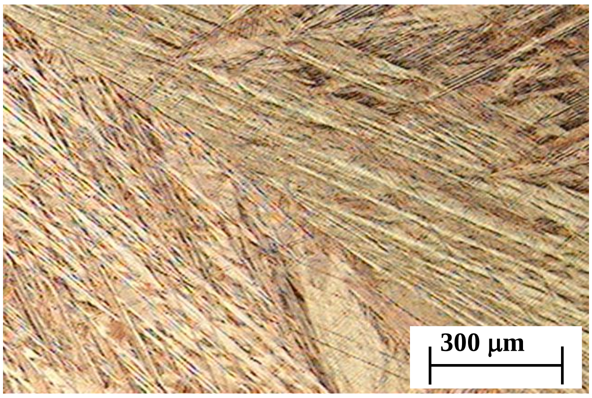

Figure 8. Optical microscopy micrographs of Cu-14Al-4Ni alloy submitted to aging treatment at 790 °C for 2 hours with subsequent cooling in water. Attack with ferric perchlorate solution at 5%.

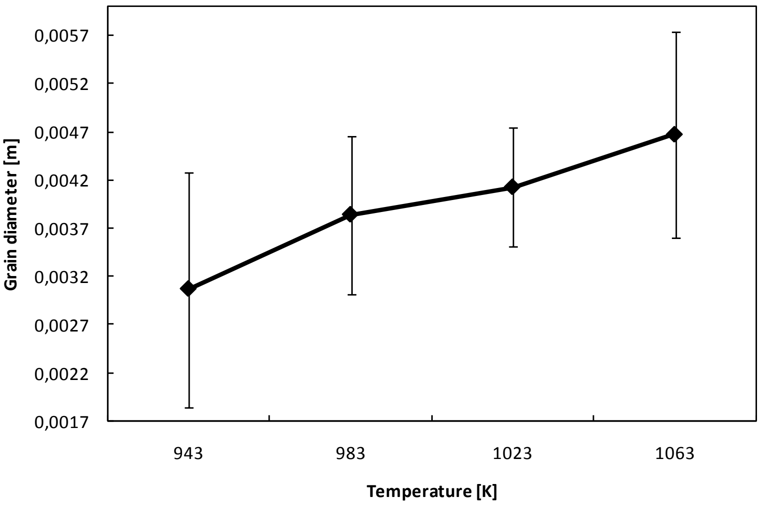

Figure 9. Graph of grain sizes in function of the aging temperatures.

For all conditions studied (temperatures treatment) was found in a high dispersion results in relation to size of the grains (Fig. 9). This occurs because during the solidification of the ingot (in open ingot mold metal), as the matrix wall is cold, the melted metal that leans against the wall of the matrix solidifies quickly, causing the growth of columnar grains into the center of the ingot . This generates a large compositional and morphological heterogeneity (due to different melting points of components), even when the ingot is thermomechanically processed and partially recrystallized. In addition, the grain growth in CuAlNi system alloys is favored by low values of activation energy of the growth process. At high temperatures (above 600ºC) the secondary recrystallization is easily observed (due to high atomic diffusion through grain boundaries), characterized by the declivity in the diagram *ln [D-D$_0$] x 1/T* and the morphology of some grains.

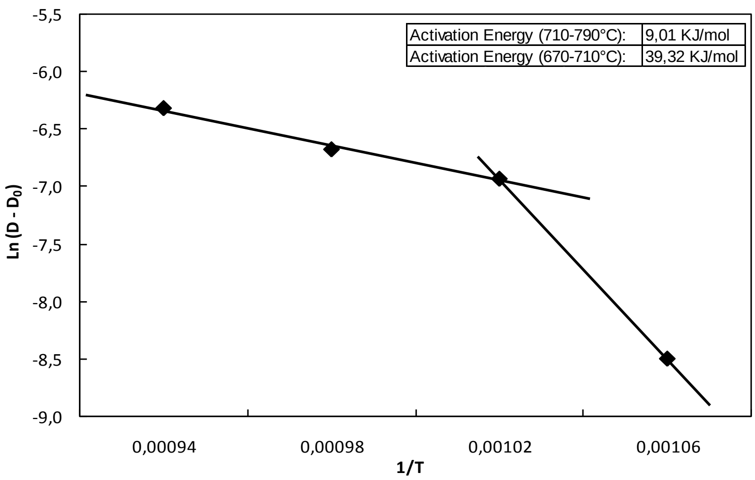

Figure 10. Diagram ln [D-D$_0$] x 1/T for determination of activation energy of grain growth process.

The results showed that the Cu-14Al-4Ni alloy is extremely sensitive to temperature variation in which the alloy is treated, having a dual kinetics of grain growth, where, through the diagram *ln [D-D$_0$] x 1/T*, the empirical activation energy process was estimated for two domains of growth (Fig.10). In the first domain, between 670 and 710ºC (943 and 983 K), the declivity of the line gives us a value for the activation energy equal to 39.32 KJ/mol, in the second domain, between 710 and 790ºC (983 and 1063 K), the declivity of the line gives us a value for the activation energy equal to 9.01 KJ/mol. Similar behavior has been observed in alloy of the CuZnAl system (Lima, 2000 and Ferreira, 1998).

4. CONCLUSIONS

The Cu-14Al-4Ni alloy is extremely sensitive to temperature variation in which the alloy is treated, having a dual kinetics of grain growth. This behavior presented by this alloy, similar to what occurs with other alloy systems (CuZnAl and CuAlBe), may be associated, in the first domain, of lower temperature, to primary recrystallization (involving a higher activation energy), and the second domain, of higher temperatures, to secondary recrystallization, produced by intense atomic diffusion through contour (involving a lower activation energy).

5. ACKNOWLEDGEMENTS

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