Grain Size and Temperature Influence on the Toughness of a CuAlBe Shape Memory Alloy

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Abstract

This work is a study of the influence of grain size and temperature on the toughness of CuAlBe shape memory alloys with (CuAlBeNbNi) and without NbNi (CuAlBe) grain refiner elements. The toughness analysis was based on the V-notch Charpy impact test under temperatures of -150, -100, -50, 0, 50, 100 and 150 °C. A statistical analysis of the results led to the conclusion that the toughness of both alloys was influenced by temperature and grain size. The CuAlBeNbNi alloy absorbed higher impact energy than the CuAlBe alloy showing that the refining elements improved the toughness of the alloy. To confirm and complement these findings, the fracture surfaces were evaluated by stereomicroscopy. Smooth homogeneous surfaces and rough heterogenous surfaces were detected for the CuAlBeNbNi and CuAlBe alloys, respectively. Predominately brittle zones were confirmed by scanning electron microscopy in both alloys. Furthermore, to determine the phase transformation temperatures and the associated microstructures, the alloys were assessed by conventional differential scanning calorimetry (DSC) and DSC with optical microscopy.

**Keywords**: CuAlBe shape memory alloy; grain refiners; toughness; phase transformation temperatures; Charpy impact test; statistical variational analysis.
1. Introduction

Artificial smart structures are inspired by nature to reproduce the characteristics of natural intelligent systems. Among other domains, computer sciences, bioengineering, aerospace engineering and industrial automation are exploring the unique characteristics of natural intelligent systems.

The design philosophy of artificial smart structures is based on the analysis of parameters that can be adjusted so that the structures respond to external stimulus in a competent manner. These structures are built from smart materials, like shape memory alloys that are commonly used, for example, in sensors [1] and actuators [2].

Similar to all shape memory alloys, the ternary CuAlBe shape memory alloy (SMA) presents exceptional mechanical characteristics, such as its capacity to return to the original shape and/or size after severe thermal variations, and its high pseudo elastic strain [3]. Other important characteristics include superelasticity, strong damping effect, excellent capacity to absorb sound, vibration and mechanical waves due to its coarse grain size [4], high mechanical strength, superior resistance to corrosion [5], low manufacturing costs, ease of manufacturing as well as its good usability at low temperatures. These outstanding characteristics justify its widespread use in numerous applications, such as pipe joining in the petroleum industry, as an efficient alternative to traditional pipe welding [6], and to attenuate the effects of seismic vibrations [7, 8] and sonorous vibrations [4].

Also important is the effect of Beryllium (Be) on the characteristics of the CuAlBe shape memory alloys. It is commonly accepted that Be reduces the phase transformation temperatures. In fact, the addition of approximately 0.1% of Be, reduces these temperatures by about 100 ºC [9]. Beryllium and Copper (Cu) provide the high mechanical strength that CuAlBe alloys present when under high pressure. In addition,
Be has the highest specific heat for metallic materials, excellent thermal conductivity and outstanding mechanical properties, both at very high and cryogenic temperatures. Also, Be presents high stiffness to weight ratio that combined with its excellent damping properties makes CuAlBe alloys premier materials for acoustic applications [4].

The main motive to study CuAlBe alloys was due to their advantages in comparison to CuAlNi alloys, which suffer embrittlement at the service temperatures used for these kinds of smart materials. Also, the main competitors, the NiTi alloys, are very expensive. Potentially, there are cheaper alternative alloys, such as the CuAlZn and CuAlMn alloys. However, there are severe difficulties in controlling the chemical composition of CuAlZn alloys and the CuAlMn alloys with a high Al content present low ductility [9, 10]. Due to the disadvantages of these alternative alloys the CuAlBe alloys are used more frequently in industrial applications and are generally considered as a first-rate alternative to the NiTi shape memory alloys [9]. Furthermore, the mechanical properties of CuAlBe alloys can be improved further with the addition of grain refiner elements. These elements increase the resistance of these alloys to strain, ultimate strength and rupture stress [4].

Nowadays, many researchers are studying CuAlBe alloys. However, as these studies are relatively new there are few data and findings concerning their properties and behavior currently available. From the studies that have been carried out, the most significant ones concern the quenching treatment effect on the reversible martensitic transformation [11], the stress analysis of the martensitic transformation [12], stabilization and hyper-stabilization [13], the microstructural characterization of precipitates [14], their superelastic behavior [15] and fatigue resistance [16] and the mechanomagnetic spectroscopy of ferromagnetic SMA [17]. Other studies are mainly
related to the effect of the chemical composition of the alloys with and without the addition of grain refiner elements on the mechanical properties of the alloys, such as works presented in [4, 6].

The main goal of the work here is to evaluate the capacity of a CuAlBe alloy to absorb energy until rupture; this capacity is generally known as toughness. For this, two CuAlBe alloys, one with NbNi grain refiner elements, which are usually added to improve the mechanical properties of these alloys and another one without these elements were evaluated. The toughness was assessed using the V-notch Charpy impact tests at temperatures of -150, -100, -50, 0, 50, 100 and 150 ºC, using 3 samples of each alloy for each temperature. A statistical analysis of variance (ANOVA) was carried out on the toughness values from the Charpy impact test. The results from the Charpy impact test were complemented and validated by differential scanning calorimetry (DSC), DSC with optical microscope which used the special cooling and heating device to monitor the phase transformation temperatures proposed by Melo et al. [18], and by scanning electronic microscopy (SEM).

The authors would like to point out that this is the first work to analyze the toughness of a CuAlBe shape memory alloy based on the Charpy impact test, which makes the results presented of significant value to enhance the understanding of this new smart material.

2. Materials and Methods

The CuAlBe alloys with and without NbNi grain refiner elements were cast at room temperature, in a graphite crucible with inductive heating in an 8 kVA high frequency furnace, and poured into a round chill. Then, the alloys were homogenized at 850 ºC for 12 hours in an electrical resistance furnace and water quenched under
moderate agitation at room temperature. The samples studied were obtained from the pouring gates indicated by black rectangles in Figure 1, since the central poring gate and the base of the poring gates (red rectangles) are more susceptible to the presence of pores, which cause a decrease in the mechanical properties of many shape memory alloys [19, 20]. Afterwards, the alloys were machined and again water quenched under ambient atmosphere to recover the shape memory effect. The experimental work carried out is explained in detail below.

Metallographic analyses were carried out on the samples to assess the efficiency of NbNi refining elements to reduce the grain size of the CuAlBe alloy. For the analyses the alloy samples were first cleaned, polished and chemically etched with ferric chloride (FeCl3) for 10 seconds.

Conventional differential scanning calorimetry (DSC) tests were carried out on the CuAlBe alloys with and without NbNi grain refiners to determine the phase transformation temperatures, as well as the phases present at each temperature used. For these tests the samples, measuring Ø5x1.5 mm^2 and weighing around 215 mg, were heated and cooled at a 10 K/min rate by a 50 ml/min constant nitrogen gas flow.

The alloys were machined according to the ASTM E 23-96 [21] standard for the Charpy impact test, for which the dimensions of the samples should be 55x10x10 mm^3 and the V-notch should have a bend radius of 0.25 mm, 2 mm depth and an angle of 30°. The V-notch is the most important parameter to be considered in this kind of mechanical test and was machined using an electrical cutting tool specifically designed for this purpose. Finally, the samples were submitted to another heat treatment to obtain the shape memory effect [6, 10]. Toughness of the samples was analyzed at temperatures of -150, -100, -50, 0, 50, 100 and 150 °C. For temperatures lower than 50 °C, liquid nitrogen was used and the samples were stored in a thermal recipient. To heat
the alloy samples to temperatures greater than 0 °C, a constant flow of hot air, supplied by a thermal industrial blower, was used.

To avoid undesirable heat losses when positioning the samples in the Charpy impact testing machine, a special stainless steel positioning device was used. To determine the temperature variations of the alloy samples, a Chromel-Alumel thermocouple connected to a millivoltmeter registered the temperatures at which the toughness values were obtained.

After the Charpy impact tests, the alloy samples were analyzed at room temperature through a DSC using optical microscopy [18]. Liquid nitrogen was used for cooling the samples and a constant alcohol flow was used for heating the samples. The samples were immersed in ethyl alcohol to avoid water condensation that causes the blurring of acquired images. The phase transformation temperature variations of the samples were assessed using a Chromel-Alumel thermocouple connected to a millivoltmeter with output to a microcomputer for their posterior analysis and correlation with the chemically etched images observed and acquired by optical microscopy. Therefore, accurate and reliable synchronization between the image acquisition processes and the temperatures of the phase transformations was guaranteed [18].

3. Results and Discussion

As mentioned, the metallographic analyses of the CuAlBe and CuAlBeNbNi alloys were carried out at room temperature to evaluate, microscopically, the effect of the NbNi grain refiner elements on the microstructure. This evaluation confirmed that both alloys only presented the austenite phase and that the addition of the refiner elements reduced the average grain size from 1950.00 µm to 100.77 µm, as can be seen
in Figures 2a and b, respectively. Additionally, these findings were confirmed by performing 60 HMV-2 micro hardness tests (Shimadzu, Kyoto, Japan) on the two alloys. The grain size refinement upon adding Nb is thought to be due to the formation of fine Nb-rich precipitates that act as nucleation sites in the solidification process. Moreover, the Nb-rich precipitates inhibit further grain growth during the high temperature homogenization heat treatment by the pinning mechanism, which is favored by the negligible solubility of Nb in the matrix. Furthermore, Lelatko and Morawiec [22], identified these particles as being Nb(Cu,Al)2 precipitates by transmission electron microscopy (TEM). The grain size reducing effect improves the mechanical properties of this alloy considerably, acting as a strengthening mechanism as was described by Montecinos et al. [7] and Araya et al. [8].

Following the microstructural evaluation, the samples underwent differential scanning calorimetry (DSC) to measure their phase transformation temperatures, as well as to determine the phases at each temperature used in the Charpy impact test. Figure 3 shows the DSC curves obtained for the CuAlBe with (in red) and without (in black) NbNi grain refiner elements during heating and cooling between -120 and 150 °C. This Figure shows two peaks during the heating and cooling processes. Based on these peaks, it is possible to obtain the phase transformation temperature zones (PTZ) that are indicated in Figure 3 as As and Af - starting and finishing of the martensitic to austenitic phase transformation, and as Ms and Mf - starting and finishing of the austenic to martensitic phase transformation, respectively. As these phase transformation temperatures are defined, the DSC profile for the CuAlBe alloy can be considered stable.

In the Charpy impact tests for temperatures greater than 0 °C, the samples were heated with an industrial blower up to 190 °C and then allowed to cool naturally until
the desired test temperature. For temperatures lower than 50 °C, the samples were cooled using liquid nitrogen to -190 °C and then allowed to heat up naturally to temperatures of -150, -100, -50 and 0 °C. The heating curve in Figure 3 shows the temperatures for As and Af that correspond to the austenitic to martensitic phase transformations as approximately -56 and -25 °C for the CuAlBeNbNi alloy (represented in red), and -91 and -45 °C for the CuAlBe alloy without NbNi (represented in black), respectively.

Table 1 shows the toughness values, i.e. the absorbed energy for the CuAlBeNbNi alloy samples. The highest averaged toughness, equal to 15.4 J, was obtained at around -50 °C, a temperature at which the process of transformation from martensite phase to austenite phase had already started, and was therefore made up of two-phases (austenite and martensite). All the other test temperatures gave toughness values very close to each other. For all the test temperatures used, except for the -50 °C temperature, the phases were fully defined: at temperatures of -150 and -100 °C, only the martensite phase was present, and from 0 to 150 °C only the austenite phase was present (Figure 3).

The results obtained by Brachet et al. [23] from Charpy impact tests on a Ti50Ni50 shape memory alloy showed that this material, which has superior mechanical properties to the CuAlBe alloys but is much more expensive, reaches toughness values of 5 J. This value is lower than all the toughness values obtained in this work: the lowest value was 11.5 J, which was obtained at the temperature of +100 °C, and the global average toughness value was 12.7 J. Also, Albuquerque et al. [24] and Silva et al. [25], studied an AISI 4140 steel, which is frequently used in pipe welding, and they obtained a toughness value of around 20 J. Therefore, the CuAlBeNbNi alloy studied here revealed toughnesses close to or even better than other metallic alloys usually used in industrial applications. It is important to note that, as far as the authors know, there
are no previous works analyzing the capacity of CuAlBe alloys to absorb energy until
t heir rupture, which is one of the main contributions of the experimental work of this
paper.

The analysis by scanning electron microscopy (SEM) revealed that all samples
showed regions of cleavage, (Figure 4a), and also typical brittle fracture regions,
(Figure 4b). Figures 4c and d show two fracture micrographs from SEM of the CuAlBe
alloy, where the cleavage regions are just noticeable. This was verified for all the
temperatures studied. These findings were also obtained by Siredey and Eberhardt [16],
when analyzing the fatigue behavior of a CuAlBe alloy, and by Wang et al. [26] when
studying the compact tension in a NiTi alloy. However, in our work, dimple zones were
only observed in the CuAlBeNbNi alloy at the temperature of -50 ºC.

For the temperature of -50 ºC, as well as for all the other temperatures evaluated,
stereomicroscopy revealed brittle fractures on very homogeneous surfaces of the
CuAlBeNbNi alloy samples (Figure 5a). However, at the temperature of -50 ºC, which
is associated with a region made up of two-phases, small regions along the edges of the
samples showed zones with dimples, typical of ductile fractures (Figure 5b). The
toughness of the -50 ºC samples was higher than for the other test temperatures due to
these dimple zones. All the other regions of the -50 ºC samples were cleavage zones
relating this temperature to brittle. Only cleavage zones were detected at the
temperatures of -150, -100, 0, 50, 100 and 150 ºC (Figures 5c to i, respectively). At the
temperature of -50 ºC, the phase transformation zone of the CuAlBeNbNi alloy is
associated to a high damping effect [27], which also justifies the high toughness value
observed.

Table 2 shows the toughness values of the CuAlBe alloy without NbNi grain
refiner elements. As expected, based on the analysis of the metallographic images
acquired (Figure 2) and also on the DSC results (Figure 3), the CuAlBe alloy without NbNi grain refiner elements revealed a considerably inferior toughness compared to the CuAlBeNbNi alloy. This behavior is because the CuAlBeNbNi alloy has a larger amount of grain boundaries due to refining achieved by adding the NbNi elements. These contours act as barriers that hinder crack propagation during impact testing as has been reported over the years, for example [28, 29]. Thus, in many cases, the fracture resistance of a brittle material is dominated by the grain boundary toughness, instead of the fracture resistance of the crystallographic planes [30]. Thus, the CuAlBe alloy without NbNi refining elements has characteristics of coarse grain size materials that are considered to be more brittle. This proves that the smaller grain size increases mechanical properties of the metallic alloys as was previously confirmed by Albuquerque et al. [4] regarding the CuAlBe alloy.

Analyses based on stereomicroscopy (Figure 6a) and SEM (Figure 6b) were also carried out on the samples which confirmed that the CuAlBe alloy without grain refiners has inferior toughness values compared to the corresponding alloy with grain refiners, as well as an irregular fracture surface.

The samples were also submitted to DSC based on optical microscopy to monitor the phase transformations and to compare their temperatures to the ones obtained by conventional DSC, as well as to confirm the phases present at each temperature studied. For the CuAlBeNbNi alloy, this procedure led to values of approximately -26 and -52 °C as the Af and As temperatures, respectively. These values showed a difference of 1 and 4 °C for the Af and As temperatures obtained by the conventional DSC. The values determined by both methods are very similar, showing the efficiency of the method proposed by Melo et al. [18] to micro-structurally monitor the temperatures of phase transformations. Figure 7 shows the micrographs obtained by DSC microscopy. These
images show the martensite (Figure 7a), martensite-austenite (Figure 7b) and austenite phases (Figure 7c) at temperatures of -100, -50 and 0 ºC, respectively, used during the heating process of the CuAlBeNiNb alloy.

To statistically validate the results of the Charpy impact tests, ANOVA analysis was carried out using STATISTICA software (StatSoft, Inc., USA). ANOVA is based on the function of probability (F) obtained from a set of experimental data [31]; in this work: temperature and toughness. For the temperature values used in the experimental work and considering a confidence level of 99.25%, ANOVA confirmed that the toughness of the CuAlBeNbNi alloy is influenced by temperature (Table 3). Figure 8 graphically represents the results obtained for the toughness of the CuAlBeNbNi alloy from the data presented in Table 1. In this Figure, the vertical bars denote confidence intervals of 0.95 for the current effect of F (6, 14) = 4.7789 and p = 0.00750. However, if the temperature of -50 ºC, responsible by the highest toughness value is not considered in the statistical analysis, then the confidence level decreases to approximately 52.02%, and toughness becomes independent of temperature (Table 4). Thus, the temperature of -50 ºC was relevant for this study of the CuAlBeNbNi alloy.

For the CuAlBe without NbNi grain refiner elements, a statistical confidence level of 83 % was achieved by the ANOVA and concluded that the toughness was independent of temperature (Table 5). However, the temperature responsible for the higher damping capacity of the alloy without grain refiner elements is approximately equal to -60 ºC (from the heating curve). The Charpy impact test was carried out at this temperature and gave toughness values equal to 4.3, 4.3 and 4.4 J, which corresponds to an average value of around 4.3 J, i.e., the highest toughness value for the CuAlBe alloy without NbNi. This reveals that a region made up of two different crystalline structures, austenite and martensite phases, absorbs more energy. Nevertheless, for the CuAlBe
alloy the absorbed energy is almost invariant with the temperature when compared with the same region of the CuAlBeNbNi alloy. This is because the CuAlBeNbNi alloy presents higher grain density, which is responsible for the increase in toughness, and is more significant in regions made up of two different crystalline structures. In addition, a brittle fracture surface was observed on the sample tested at -60 °C that only presented cleavage zones as was observed at all temperatures studied. When this temperature was added to the ANOVA analysis, the toughness became statistically dependent on the temperature values used with a confidence level of 99.39%.

4. Conclusions

An evaluation of the capacity to absorb energy until rupture, usually known as toughness, based on Charpy impact test was carried out on a CuAlBe shape memory alloy with and without NbNi grain refiner elements. This is the first time that a CuAlBe alloy has been evaluated with this goal. Complementary analyses were performed by conventional and microscopy differential scanning calorimetry and then correlated with the results from the impact test. Also, scanning electronic microscopy and optical microscopy analyses were carried out.

From the results obtained and from the analyses performed, it is possible to conclude that:

1) Optical microscopy revealed that the NbNi elements refined the grains of the CuAlBe alloy considerably, since this alloy without grain refiners had grains 19.35 times larger than the CuAlBeNbNi alloy. This reduction in the grain size significantly improves the mechanical properties of this alloy as is indicated in the current literature and confirmed in this work.
2) Conventional DSC analysis was able to determine the temperatures of the phase transformations of the CuAlBe alloy, and to confirm the appropriateness of the temperatures adopted in the Charpy impact tests. Additionally, an excellent stability during the heating and cooling processes was noted in both alloys.

3) The Charpy impact test indicated that the CuAlBe alloy with and without NbNi presented brittle behavior, and that the temperature of -50 ºC, associated to the phase transformation of the CuAlBeNbNi alloy, presented the highest toughness value and a small amount of dimples. The toughness values of the other tested temperatures were approximately equal and inferior.

4) By using DSC microscopy, it was possible to identify the microstructures of the CuAlBeNbNi alloy during the phase transformations, and correlate the temperatures and the associated microstructures. The values obtained from DSC microscopy were closer to each other than the ones obtained by conventional DSC.

5) By ANOVA analysis and under the test conditions adopted for the Charpy impact test a confidence level higher that 95% was obtained for the results of both alloys. The analysis showed that the CuAlBeNbNi alloy toughness values were not constant and were affected by temperature. The temperature of -50 ºC had the greatest effect on toughness variation. The same behavior was not observed for the CuAlBe alloy, as the toughness revealed to be independent of temperature. However, when the temperature of -60 ºC, a region of austenite and martensite phases, was evaluated for toughness a different value was found, indicating that the toughness of the CuAlBe alloy could also be affected by temperature.

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Additionally, the first author thanks CNPq – Conselho Nacional de Desenvolvimento Científico e Tecnológico (National Counsel of Technological and Scientific Development), in Brazil.

References


FIGURE CAPTIONS

Figure 1: CuAlBe as-cast.

Figure 2: Microphotographs of CuAlBe alloys a) without and b) with NbNi grain refiner elements.

Figure 3: DSC curves during heating and cooling: Ms and Mf are the starting and finishing of the martensitic to austenitic phase transformation, As and Af are the starting and finishing of the austenitic to martensitic phase transformation, and PTZ are the phase transformation temperature zones, respectively.

Figure 4: SEM obtained from the CuAlBeNbNi alloy: a) cleavage region at -100 ºC and b) typical region of a brittle fracture at -150 ºC; and from the CuAlBe alloy: c) cleavage region at -100 ºC and d) characteristic region of a brittle fracture at -150 ºC.

Figure 5: Brittle fracture in the CuAlBeNbNi alloy at -50 ºC: a) fracture surface from stereomicroscopy, b) dimples and c) cleavage regions from SEM; d) to i), cleavage regions that were verified at the temperatures of -150, -100, 0, 50, 100 and 150 ºC, respectively.

Figure 6: Aspect of a brittle fracture in a CuAlBe alloy without NbNi grain refiner elements by: a) stereomicroscopy and b) SEM evaluation.

Figure 7: Microstructures obtained from DSC microscopy (As and Af are the temperatures associated to the austenitic to martensitic phase transformation) in the CuALBeNbNi alloy: a) martensite, b) martensite-austenite and c) austenite.

Figure 8: Toughness values for the CuAlBeNbNi alloy (the circles represent the average values and the vertical bars denote confidence intervals of 95%).
TABLE CAPTIONS

Table 1: Toughness of the CuAlBeNbNi alloy.
Table 2: Toughness of the CuAlBe alloy without NbNi grain refiner elements.
Table 3: Results of the ANOVA analysis on the Charpy impact test results of the CuAlBeNbNi alloy.
Table 4: Results of the ANOVA analysis on the Charpy impact test results of the CuAlBeNbNi alloy at all temperatures analyzed except the temperature of -50 ºC.
Table 5: Results of the ANOVA analysis on the Charpy impact test results of the CuAlBe alloy at all temperatures analyzed.
Figure 2b

Figure 3
Figure 8

The graph shows the absorbed energy [J] as a function of test temperature [°C]. The peaks and troughs indicate varying energy absorption across different temperature ranges.
### Table 1

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<td>$p$</td>
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