AGING STUDY IN A Cu-Al-Mn SHAPE MEMORY ALLOY

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Abstract: *A great obstacle for technological applications of the shape memory effect is the degradation of the phenomenon due to the martensitic stabilization processes. The martensitic aging induces alterations in the shape memory effect resulting in important modifications in the physical-mechanical behaviours. Martensitic stabilization can be eliminated or lessened through specific thermal treatments or addition of new element alloys (chemical). The study of aging (stabilization process) involves also martensite/marensite and austenite/martensite interfaces displacement behaviours and critical stress induced transformation. In this work, a Cu-10Al-8,4Mn (%wt) shape memory alloy obtained in an induction furnace has been studied. The thermal treatments given to the samples were: homogenisation at 850^{0}C for 15 minutes and betatization (A- quenched in water at room temperature, B- quenched in water at 100^{o}C and C- air quenched). The characterization of the samples was carried out by means of optical microscopy (microstructure), X-rays diffraction (crystalline structures) and electrical resistivity changes (transformation temperatures). The results are discussed in terms of thermal treatment influences and stabilization processes. Experimental procedure modifications are proposed to reduce the problems caused by aging of cooper-based shape memory alloys.*

Keywords: *Shape memory alloys, Cu-Al-Mn alloys, martensitic stabilization.*

1. Introduction

Shape memory alloys (SMA) are non-conventional functional materials that present a large domain of potential applications based on its thermoelastic properties: shape memory effect (SME - one way), reversible shape memory effect (SME - two way), pseudo elasticity (superelasticity and rubber like behaviour) and high capacity of damping. The origin of these effects is the thermoelastic reversible martensitic transformation. This transformation occurs without diffusion (first order), with homogeneous deformation of the crystalline structure and is constituted essentially by a shear stress (Otsuka & Shimizu, 1986 and Petty, 1970). A great obstacle for the technological applications of the SMA is the martensitic stabilization process. Martensitic stabilization is related to several aspects, such as: thermal treatment, chemical composition, time below M_S and others. The stabilization degrades SME properties (loss of memory/amnesia), presenting its effects in several ways: changes in the transformation temperatures, decrease of transformed martensite fraction, alterations and irregularities of physical and mechanical measurements during the transformation, decrease of damping coefficient and increment of elastic module in relation to not stabilized martensite and others (Mantel et al., 1998 and Ahlers, 1986). Main mechanisms of stabilization are the pinning of interfaces by quenched-in vacancies, martensitic structure modification and degree of order of austenite retained after quench (Gonzalez et al. 2004).

The objective of this work is to study the martensitic stabilisation in a Cu-Al-Mn SMA submitted to three types of thermal treatments: quenched in water, quenched at 100^{o}C and air quenched. The results of the transformation temperatures behaviour and transformed fraction changes are analyzed in function of thermal treatments influences and stabilization processes.

2. Experimental procedures

The selected cooper-based alloy has a nominal chemical composition of Cu-81,6% Al-10% Mn-8,4% in weight percent. This composition was chosen because the critical transformation temperatures (M_S, M_F, A_S and A_F) are highest that the room temperature. The Cu-Al-Mn alloy was prepared from chemical elements of high purity in an induction-melting furnace (24 KVa). Ingot was homogenized in a resistance furnace at 850ºC for 24 hours. Samples were cut into rectangular primes, using a low speed diamond saw, for the following dimensions: length = 25 mm, width = 5 mm and thickness = 1.5 mm. Surface deformed layers were eliminated by chemical etching in an aqueous solution of 15% HNO_3. To exhibit the shape memory effect, the cooper-based SMA should be submitted to a betatization thermal treatment. This treatment consists of maintenance in the β-phase domain (850°C) for 15 minutes, followed by quench to retain the β_1 metastable phase. The samples were submitted to three different quench thermal treatments: A - quenched in water at room temperature (Q25), B - quenched in water at 100^{o}C with annealing at 100^{o}C (Q100) and C - air quenched (AQ). Microstructure of samples was observed by optic microscopy with polarized light and Normanski contrast. The crystalline structure was characterized by X-ray diffraction (XRD) using Cu-Kα radiation (λ = 1,54184Å).

The critical transformation temperatures were determined by electrical resistivity (ER) measurements versus temperature using a conventional four terminals method. For these measurements, a constant electrical current (*i*) pass through the sample and two conduct wires are spot-welded on the sample for the measurement of the voltage signal (ΔV), as shown in Fig. 1. As electrical current is always constant, ER changes as a function of temperature and the phase transformation temperatures are determined. The temperature of sample is controlled by keeping it into a silicone oil bath with forced circulation. This system allows thermal cycles between 0 and 200^{o}C.

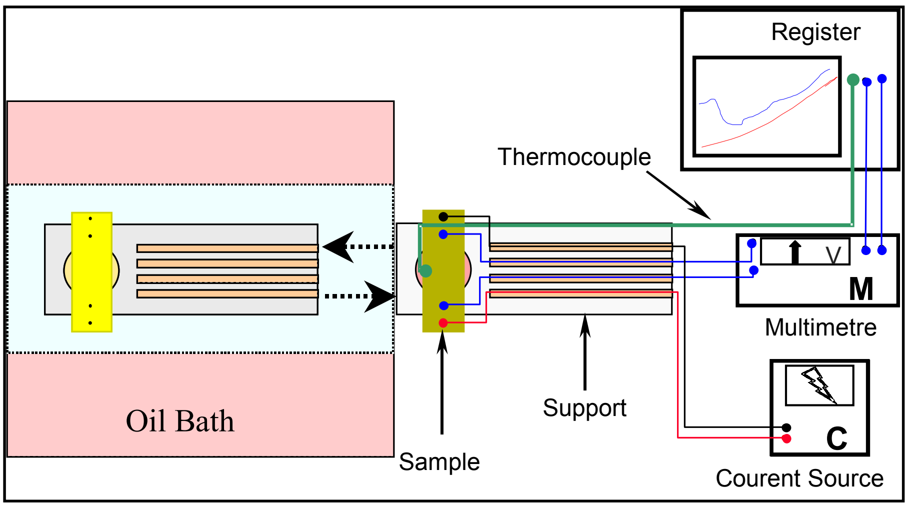


Figure 1 – Schematic representation of the system for electrical resistance measurements.

Figure 2 shows a schematic typical curve of ER versus temperature where are represented the characteristic parameters of the thermoelastic martensitic transformation. Inflexion points (tangent method) define the phase transformation temperatures. During cooling, M_S and M_F temperatures correspond to the start and finish of the forward martensitic transformation. During heating, occurs the inverse transformation where A_S and A_F are the reverse martensitic phase transformation temperatures. The A_{50} and M_{50} temperatures correspond to a transformation fraction of 50% in austenitic and martensitic phase, respectively. Thermal hysteresis is the difference between A_{50} and M_{50}

temperatures. Thermal amplitudes correspond to a variation of temperature (e_r and e_c) as defined in Fig.2. In summary, these parameters of figure 2 are represented as follow below:

α - martensite fraction transformed
M_S - start martensitic transformation temperature
M_F - finish martensitic transformation temperature
M_{50} - 50% martensite fraction transformed
A_S - start austenitic transformation temperature
A_F - finish austenitic transformation temperature
A_{50} - 50% austenitic fraction transformed
H_T – transformation thermal hysteresis ($H_T = A_{50} - M_{50}$)
e_r – thermal amplitude at cooling ($e_r = M_F - M_S$)
e_c – thermal amplitude at heating ($e_c = A_F - A_S$)

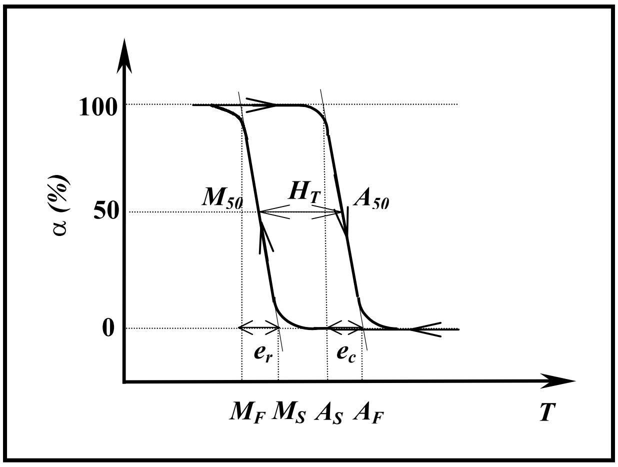
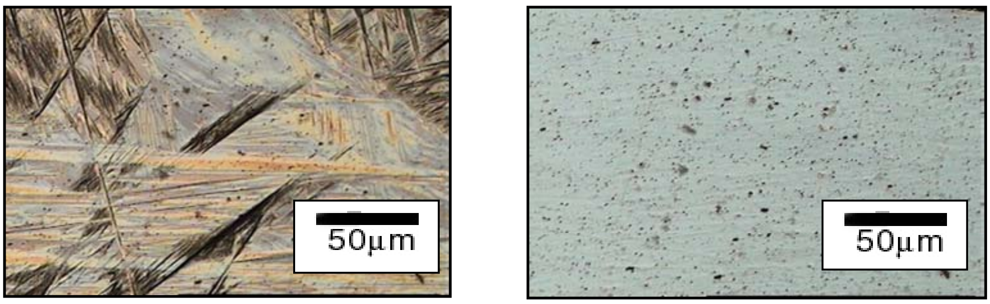


Figure 2 - Representation of characteristic parameters of the martensitic transformation.

3. Results and discussions

Figure 3 shows optical micrographs of a sample submitted to Q100 treatment. The micrographs were taken from the same pre-polished field at the indicated temperatures during heating. The microstructure observed in Fig.3(a) is characteristic of the martensitic phase due to the presence of self-accommodation needles and to the surface relief (martensite plakes). The Figure 4 presents an x-ray diffraction pattern for the Q100 sample which confirms β'_1 or 18R martensitic structure (Lee & Kim, 1990). During heating of the sample directly in the microscope, martensite needles disappears (around 95°C), characterizing the inverse martensitic transformation. Then, Fig.3(b) show the new phase that is called austenite or matrix (β_1) with order structure DO_3.



a) 25°C b) 95°C

Figure 3 - Optical micrographs of a Cu-Al-Mn sample annealed at 850°C for 15 minutes, then quenched in water at 25°C: a) martensitic phase - polarized light - 25°C and b) austenitic phase - 95°C.

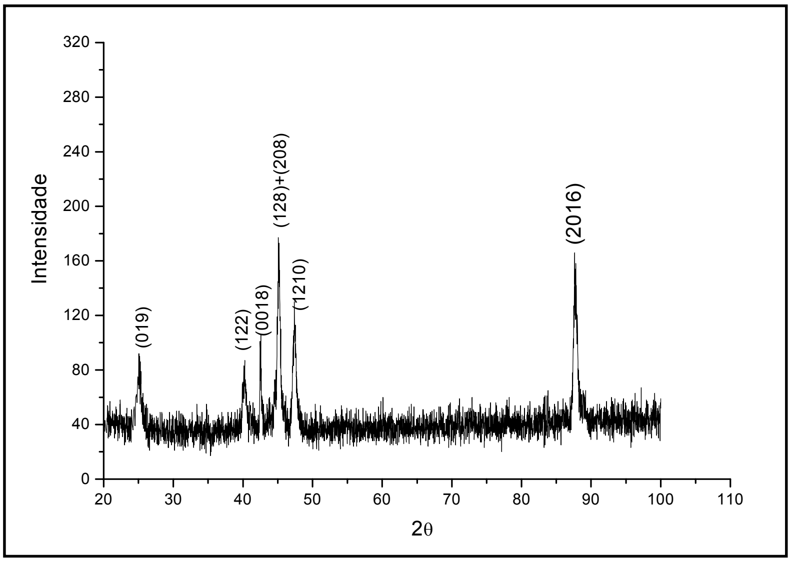


Figure 4 - XRD pattern of the studied Cu-Al-Mn alloy (martensitic phase).

Figure 5 shows ER versus temperature curves for the first thermal cycle of samples submitted to the three thermal treatments (Q25, Q100 and AQ). The behaviours of the ER curves are different for each thermal treatment, resulting in modifications of critical temperatures, transformation hysteresis and thermal amplitudes. The parameters determined for each heat treatment are: $A_S = 78^oC$, $A_F = 144^oC$, $M_S = 114^oC$, $M_F = 45^oC$, $H_T = 31{,}5^oC$ and $e_H = 66^oC$ for the Q25 sample; $A_S = 72^oC$, $A_F = 104^oC$, $M_S = 95^oC$, $M_F = 48^oC$, $H_T = 16{,}5^oC$ and $e_H = 36^oC$ for the Q100; $A_S = 52^oC$, $A_F = 91^oC$, $M_S = 76^oC$, $M_F = 38^oC$, $H_T = 14{,}5^oC$ and $e_H = 39^oC$ for the AQ sample. Values of thermal amplitude during heating (e_H) and thermal hysteresis have important differences, mainly for the treatments Q25 and AQ.

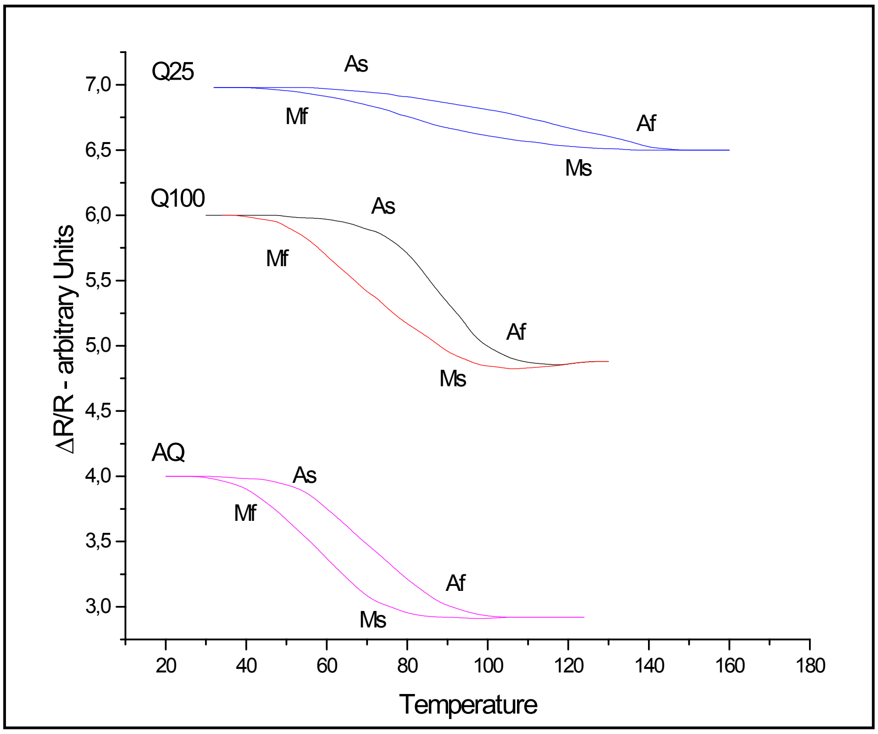


Figure 5 – ER versus temperature curves for the Cu-10Al-8,4Mn alloy submitted to heat treatments: Q25, Q100 e AQ. Phase transformation temperatures are indicated.

Figure 6 are shows ER x T curves of three thermal cycles for each thermal treatment. The curves reveal significant evolutions of the measured parameters (temperatures, hysteresis and amplitude) during thermal cycles. Experimental results obtained from Fig. 6 are summarized in Fig. 7 by means of the transformation temperatures versus number of thermal cycles behaviour. During heating, the Q25 sample presents large thermal transformation amplitude (A_S - A_F) of about 76°C, for which occurs the inverse martensitic transformation. This effect is due the supersaturation of quenched-in vacancies that pinning the martensite/austenite interfaces (Gonzalez et al. 2003). Thus, the inverse transformation needs larger energy, resulting in increase of A_F temperature.

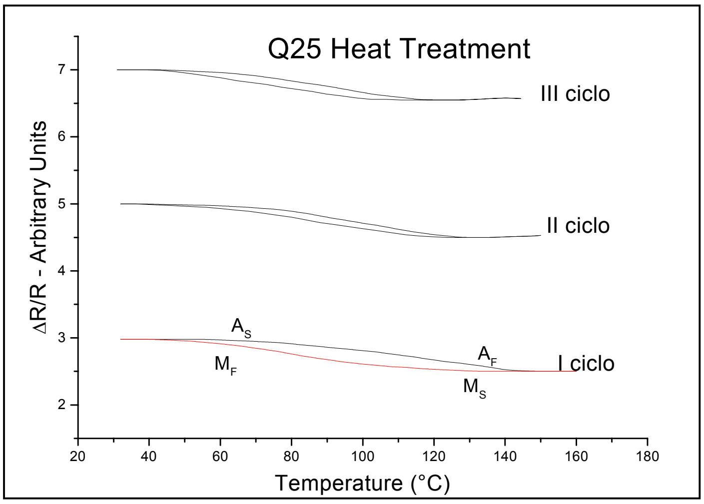


Figure 6.a

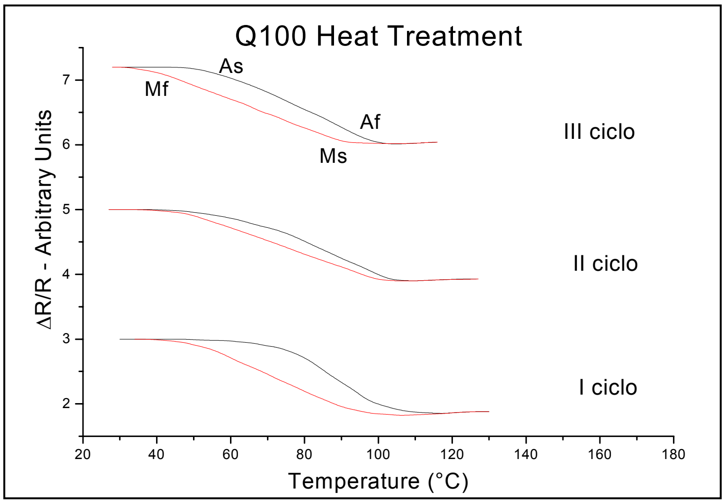


Figure 6.b

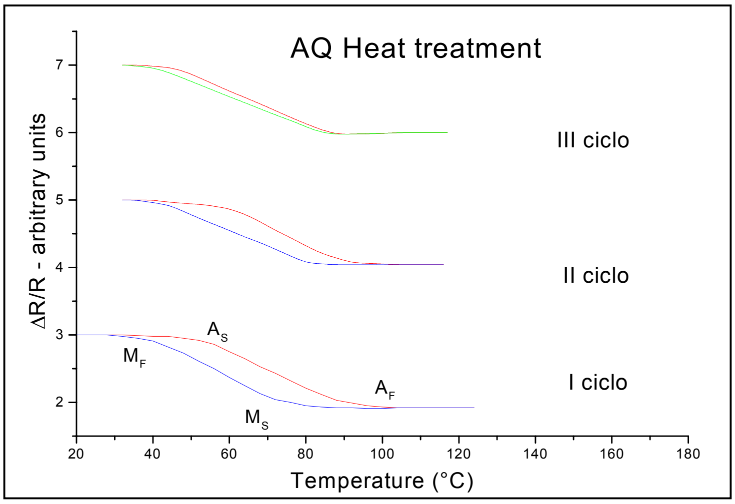


Figure 6.c

Figure 6 - Effect of thermal cycling on the transformation of the Cu-10Al-8,4Mn samples submitted to the three heat treatments: a) Q25, b) Q100 e c) AQ.

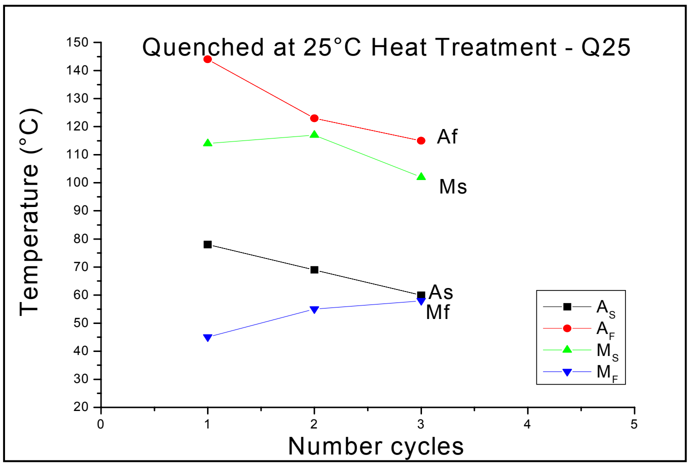


Figure 7.a

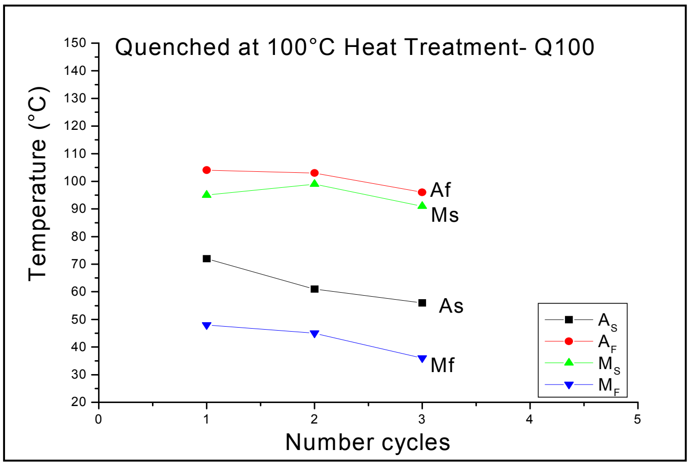


Figure 7.b

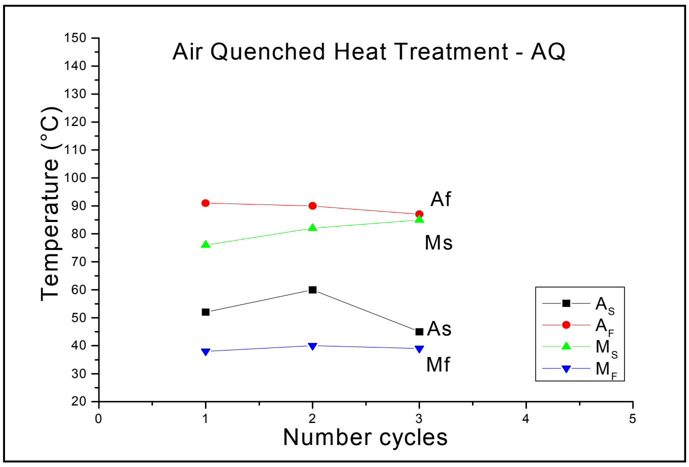


Figure 7.c

Figure 7 - Transformation temperatures versus number of thermal cycles for the Cu-10Al-8,4Mn samples submitted to the three heat treatments: a) Q25, b) Q100 e c) AQ.

For the Q100 sample, thermal amplitude is of the order 32^{o}C, indicating that the vacancy concentration is reduced for this thermal treatment. In this case, quench at 100^{o}C and annealing at 100^{o}C heat treatment leads to the elimination of quenched-in vacancies due to permanence of the material in the austenitic phase. In cooper-based SMA, mobility of the vacancies in the austenitic phase is higher than the one in martensitic phase (Benchiheub et al., 2000; Van Humbeeck et al., 1989). This maintenance of the material at 100^{o}C also increases the degree of order of the austenitic phase (DO_3) (Ahlers, 1986). The water quenched specimens (Q25 and Q100 thermal treatments) have presented a tendency of decrease in transformation temperatures and thermal hysteresis during thermal cycling. This evolution is influenced by the mechanisms of vacancies elimination, reordering phase processes and training process (martensite preferential needles).

AQ sample presents small amplitude and thermal hysteresis during the first thermal cycle. During thermal cycling, the variations of measured parameters are smaller than the ones observed in samples submitted to other thermal treatments. Thermal shock influence is smaller for this treatment compared to other thermal treatments. Thus, AQ sample present a reduced concentration of vacancies and disorder configurational phases (austenitic and martensitic). This thermal treatment accelerates the training process in the studied Cu-Al-Mn alloy. The increase of M_S and decrease of A_S temperatures is an indicative of this mechanism. For the others treatments this evolution is inverse. The Cu-Zn-Al alloys present thermal amplitudes between 10 and 15°C. In contrast, the Cu-Al-Mn shape memory alloys presents a large thermal amplitude (about 40°C), independently of the thermal treatment. This characteristic of Cu-Al-Mn alloys can increase the use of SMA in technological applications that need great difference between start and finish temperatures of direct and inverse transformation.

4. Conclusions

This work has studied stabilization processes in a Cu-Al-Mn shape memory alloy. The experimental results show that the physical characteristics of this alloy are sensitive to the type of thermal treatment employed to obtain the shape memory effect. For samples quenched in water (Q25 and Q100 heat treatments), a large influence on transformation temperatures, hysteresis and thermal amplitude are observed. These influences have been attributed to the freeze quenched-in vacancies (blockage of martensite/austenite interfaces), elimination of vacancies and reordering processes (mistake of order structure retain during quench). Moderate quench (AQ heat treatment) produce samples with more stables shape memory properties. This heat treatment reduces the problems caused by aging in the Cu-Al-Mn alloys. These alloys present large thermal amplitude that can be interesting for some technological applications.

5. Acknowledgments

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