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Microestrutural Evolution in a CuZnAl Shape Memory Alloy: Kinetics and Morphological Aspects

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The microstructural evolution of the CuZnAl shape memory alloys was studied by indirect techniques relating to the atomic migration rate of grain boundaries. Addition elements were used in a Cu-15,5Zn-8,0Al alloy to provide a comparison with the same alloy without microelement additions. The alloys were melted in an induction furnace of 24 kVA. After casting, the bulk samples of the alloys were homogenized. Then they were solution treated and hot-rolled followed by water-quenching to initiate the recrystallization. Finally, annealing produced at different temperature ranges was made in different samples 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 same empirical law of grain growth was found for the different alloys and the ln [D-D_o] x 1/T diagrams were plotted in order to establish the kinetic behavior. Based on the estimated values of the activation energy, important conclusions were obtained concerning the addition elements.

Keywords: *microstructural evolution of the CuZnAl, effect of B and Fe on the CuZnAl alloys, kinetics and morphology of CuZnAl. alloys*

1. Introduction

The alloys of the CuZnAl 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. This control can be obtained indirectly by increase of the activation energy of diffusion, which can be produced through the addition of microelements in the alloy.

After academic euphoria concerning the phenomenological aspects of the shape memory effect, researche on the physical metallurgy turned over to the microstructural control of the alloy, in an attempt to eliminating such typical problems as ageing and grain growth. The traditional method for the stabilization of the microstructures was the addition of alloy microelements. For shape memory copper-based alloys, several microelements have been used. Wang. *et al.*[1] verified the influence of zirconium, titanium, boron and iron on the refinement and the stabilization of grains in an alloy of the CuZnAl system. Morris *et al.*[2,3] verified the influence of simultaneous use of manganese and boron on the thermoelastic effects and the mechanical properties of a CuAlNi system.

For any copper alloy system, the problem is the same: determining the amount required of the microelements to be added to the alloy system, while maintaining the ability for plastic forming required for the manufacturing process. In this work, therefore, the effects of the addition of B, Fe and Ti-B will be analyzed concerning the stabilization in CuZnAl alloy systems. The final objective will be the refining and stability of the alloy, maintaining the thermoelastic effects without reducing the formability.

2. Experimental Methods

The Cu-15.5Zn-8.0Al alloy (in weight%) was first produced without addition of microelements. In order to mini-

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mize the grain growth and stabilize the microstructure, the same alloy was produced with addition of microelements such as boron (B), iron (Fe) and titanium-boron (Ti-B). The additions, in weight %, of these microelements were 0.05 and 0.08 for boron, 0.1 for iron and 0.025 for titanium-boron (Ti-B 5/1). The alloys were melted in a RF furnace of 24 kVA, using a crucible of silicon carbide. The castings were made in air, without a protective atmosphere. The melted alloys, with the respective addition elements, were chill-cast and, after solidification, they were water-cooled at 25 °C, approximately. During the melting process, the effect of the evaporation of zinc was accounted for by addition of 2.5% supplemental amount.

After casting, ingots with 15 x 30 mm section, approximately, were homogenized at 750 °C, during 24 h. Then, the ingots were hot-rolled (2%, approximately), in order to standardize the thickness. After homogenization, the alloys were solution treated at 700 °C for two hours. At this temperature, the ingots were hot-rolled 5% by steps up to 20% deformation. Following hot rolling, the ingots were water-cooled to avoid total recrystallization. The ingots, partially recrystallized, were cut in small blocks and were annealed at different temperatures (640, 670, 700 and 730 °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 ofthese specimens, heat-treated at different temperatures, were observed by optical microscope for the statistical measurements of the grain size. An approach based on the areas of the ASTM E-112 standard was used in this process.

To describe the kinetics of the grain growth the same empirical relation was found to apply for all alloys, given by the following expression:

$$D - D_o = Kt^n \qquad (1)$$

Where (D) is the diameter of the grain, (D_o) is the initial diameter, (t) is the time of treatment, (n) is the growth order and (K) is a constant. For the thermally activated process the value of (K) is given by:

$$K = K_o \, \mathrm{Exp}[-E_{AC} / RT] \qquad (2)$$

(K_o) is the frequency factor, (E_{AC}) 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 each alloy.

3. Results

3.1. Cu-15.5Zn-8.0Al alloy without addition

The values of grain diameter were measured after heat treatment at different temperatures. Results obtained previously[5] showed that the kinetics of the grain growth for this alloy system, without microelement additions, can be divided in two domains. Two separate kinetic stages are observed in this alloy system. Based on the growth law, Eq. (1), a diagram ln (D- D_o) x 1/T was plotted and the empirical activation energy (E_{Ac}) could be for each domain. For lower temperatures, 640 ≤ T < 700 °C, the value of activation energy (E_{Ac}) was estimated to be 54 kJ/mol. For higher temperatures, 700 ≤ T ≤730 °C, the value of the activation energy (E_{Ac}) was estimated to be 43 kJ/mol.

3.2. Boron addition

The Cu-15.5Zn-8.0Al alloy with addition of Boron displayed good formability, from a qualitative point of view. After solution treatment at 750 °C, both ingots having either 0.05 or 0.08% addition of boron supported cold rolling with 20% of thickness reduction, without cracking. The kinetics of grain growth revealed that the refining effect was sensibly improved when the boron content increased from 0.05% up to 0.08%. For lower temperatures, 640 °C ≤ T ≤ 700 °C, grains grow about 7% for the alloy with 0.05% boron addition and grow about 3.5% for the alloy with 0.08% boron addition, on the average.

The ln [D-Do] x 1/T diagram obtained for this alloy reveals a two domain kinetics of grain growth, as observed previously in the alloy without microelement addition. The kinetic behavior of grain growth for the alloy with 0.08% of boron addition is shown in Fig. 1. The Tto domains can be identified.

At lower temperatures, 640 °C ≤ T < 700 °C, the activation energy was estimated to be about 178 kJ/mol. At

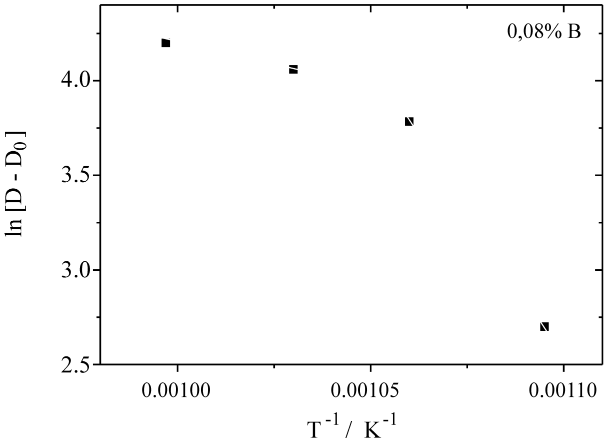

Figure 1. ln [D-Do] x 1/T diagram for the Cu-15.5Zn-8.0Al alloy with 0.08% of boron addition.

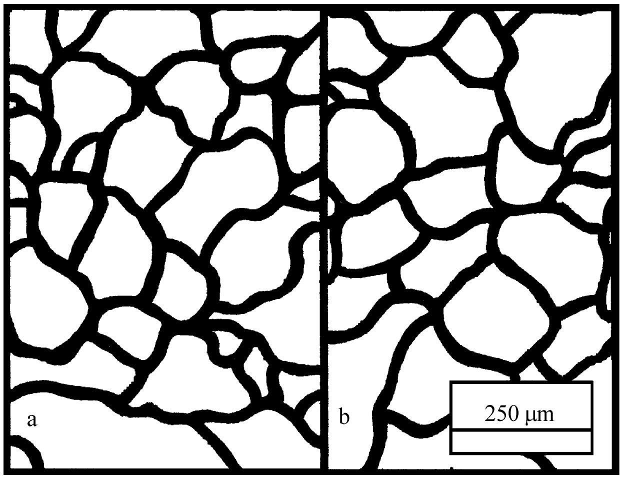

Figure 2. Grains boundaries of the Cu-15.5Zn-8.0 alloy with 0.08% of boron addition. (a) annealed at 640 °C and (b) annealed at 730 °C.

higher temperatures (T ≥ 700 °C), the activation energy decreased and was estimated at about 81 kJ/mol. Looking at the microstructure in Fig. 2, it could be observed that the addition of 0.05 or 0.08% of boron produced small and single-phase grains, apparently equiaxed, in either the chilled or central areas of the ingot (Fig. 2). Nevertheless, in central areas, where the solidification was slower, the grain growth was a little larger.

3.3. Iron addition

The iron addition with values around 0.1% in Cu-15.5Zn-8.0Al alloy considerably modified the mechanical properties. The hot-formability was decreased, so that the alloy does not support the deformation of around 20% without cracking. The efficacy of iron addition on the grain refinement was observed. The kinetics of grain growth revealed a behavior similar to the previous case, where the boron was used as an addition element. The ln [D-Do] x 1/T diagram plotted for this alloy also revealed a two domain kinetic behavoiur of grain growth (Fig. 3).

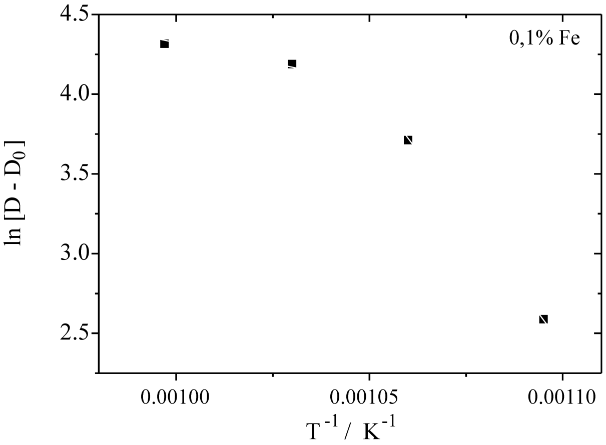

Figure 3. ln [D-Do] x 1/T diagram for the Cu-15.5Zn-8.0Al alloy with 0.1% of iron addition.

In the first domain, for lower temperatures (640° C ≤ T ≤ 700 °C) the activation energy was estimated to be 140 kJ/mol. For higher temperatures (T > 700 °C), the activation energy decreased and was estimated as 56 kJ/mol. The microstructural observations revealed that the addition of 0.1% of Fe was sufficient to produce small and equiaxed grains, with a small variation in average size. Unexpectedly, in this case the chill effect was not observed (Fig. 4).

3.4. Titanium-boron addition

In this case, the kinetics of the grain growth present a non-typical behavior in relation to the two previous cases. The great dispersion in the size of the grains produced a perturbed ln [D-Do] x 1/T diagram. Considering the high uncertainty level in the measured values of the grains, it becomes impossible to identify the two domains such as observed previously. For simple fitting of the values in the ln [D-Do] x 1/T diagram shown in (Fig. 5), the activation energy of the grain growth could be estimated at around 80 kJ/mol.

The Cu-15.5Zn-8.0Al alloy melted with the addition of 0.025% of Ti-B in the ratio t (5/1) has a considerable decrease in its hot formability in relation to the alloy with only boron addition. In spite of the decrease, it was still possible to deform this alloy by 20% in the same hot rolling process. Considering the grain refining, these results confirm a previous conclusion[5], namely that the. boron associated with the titanium is not as effective as the boron when it is used separately. The association of these two elements intensifies the directional effect during the solidification, producing oblong grains, preferentially in the areas near to the free surface, where the thermal gradients were higher (Fig. 6).

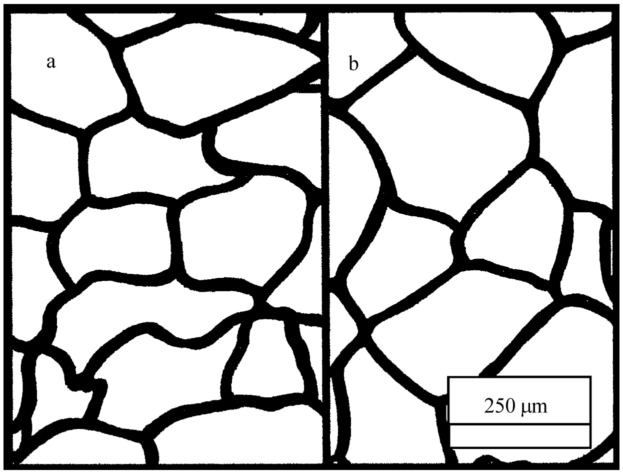

Figure 4. Grain boundaries of the Cu-15.5Zn-8.0Al alloy with 0.1% of iron addition. (a) annealed at 640 °C and (b) annealed at 730 °C.

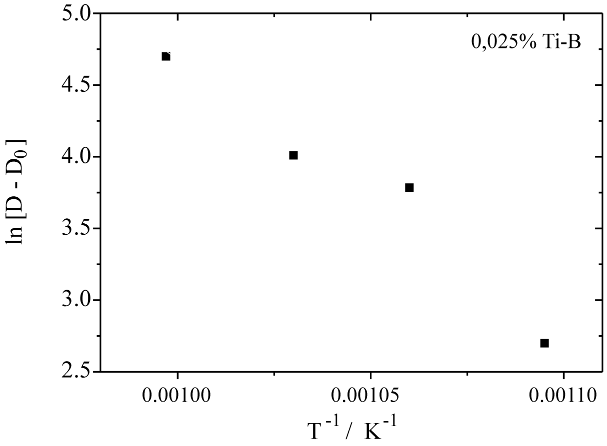

Figure 5. ln [D-D$_0$] x 1/T diagram for the Cu-15.5Zn-8.0Al alloy with 0.025% of Ti-B addition.

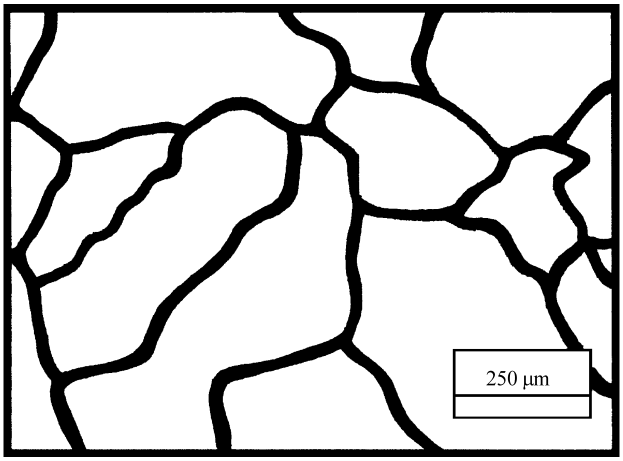

Figure 6. Grain boundaries of the alloy Cu-15.5Zn-8.0Al with 0.025% of Ti-B addition.

4. Discussion

Several authors have discussed the grain refining and grain growth behavior concerning the copper shape memory alloys. In these alloy systems, the grain refining can be produced by microelement addition[1-6]. In this work, the results showed that the CuZnAl system is extremely sensitive to the variations in the microelement content and the temperature at which the alloy is heat treated. The Arrhenius law is not observed for all conditions in the temperature domains. The results relating to the activation energy of grain growth showed that the boron was the most effective element. Its efficacy can be observed when the content increases from 0.05% up to 0.08% B. These results are not in agreement with those of Wang *et al.*[1], who observed an indifferent behavior of the boron with respect to small compositional variations. According to them, contents of up to 0.01% boron are enough to maintain the effectiveness of the grain refining in a CuZnAl system. Taking into acount the values estimated for the activation energies, our results are already quite coherent with the results obtained previously[6,7]. However, they differ from another authors for reasons linked to the chemical composition of the alloy, solidification conditions and the thermomechanical process to which we submitted our alloys and which was not used by the other authors[1,7].

In spite of being less effective than boron, iron is shown to be a good grain refining microelement in the CuZnAl alloy system The addition of 0.1% of iron produced an increment in the activation energy from 54 and 43 kJ/mol, for the alloy without addition, to 140 and 56 kJ after the iron addition. With an increase of the energy by almost three times in the domain of inferior temperatures up to 700 °C, iron becomes potentially attractive for employment in industrial scale because boron is more expensive.

Results relating to the addition of the Ti-B did not allow any conclusions to be drawn concerning the effect of grain refining. The dispersion in the size of the grains can be justified by the directional solidification character that these refining elements give to the alloy and for the high sensitivity that it acquires in relation to the thermal gradients. It is a refining addition that should be more explored for copper alloys, especially because they lack bibliographical references. However, new experiments will be necessary for a better evaluation of the parameters of the solidification.

The two domain kinetics of grain growth are observed in both alloy systems: namely the alloy without addition and alloys with iron and boron additions. Considering the events observed in both domains, the two domain kinetics can be associated, at lower temperature, to a primary recrystallization, while at higher temperatures, they can be associated to a secondary recrystallization.

The addition of microelements was certainly at the root of the increase of the activation energy for grain growth of the alloys with microelement addition, in relation to the alloy without addition. The results showed that the ideal content of each addition element depends on the chemical composition of the basic alloy. It should be neither very small so as to affect the stability of the microstructure, nor very large so as not to modify the solubility limits, where the thermoelastic properties are observed.

5. Conclusion

Boron and iron were shown to be effective in refining and stabilizing the microstructure in the Cu-15,5Zn-8,0Al alloy. The increase of the activation energy produced for each element allowed the comparison of its effectiveness in relation to the alloy without any microelement addition.

A two domain kinetic behavior of grain growth was observed in the alloy with addition of iron and boron. The values estimated for activation energy of the grain growth in each domain were, respectively, 140 and 56 kJ/mol for the alloy with iron addition and 178 and 81 kJ/mol for the alloy with boron addition.

The effects of the secondary recrystallization are larger in the alloy with addition of iron than in the alloy with boron addition. The activation energy of grain growth decreases 60% in the alloy with addition of iron, against 54% in the alloy with boron.

The results obtained with Ti-B showed that the titanium associated with t boron is not as effective as boron used separately. The result of 80 kJ/mol, estimated for activation energy of grain growth, justifies that new experiments are necessary, since the parameters of the solidification need to be controlled better.

Acknowledgments

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