

## Atomic Ordering and Martensitic Transformation in Cu-Zn-Al and Cu-Al-Ni Industrial Alloys

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**Abstract** : The isothermal relaxation process near room temperature in b Cu-Zn-Al and Cu-Zn-Al-Ni industrial alloys which follows a step quenching or an up quenching thermal treatment has been studied by isothermal calorimetric technique. The transition temperature  $M_s$  and its evolution have been obtained by differential scanning calorimetry and by detecting the acoustic emission. The dissipated energy of the sample measured during the relaxation process present a complex behaviour, characterized by a continuous slowing down. On the other hand, the evolution of  $M_s$  at the beginning of the phenomenon obeys a different law. We show that all measured evolutions are much more slow in the case of Cu-Zn-Al-Ni alloy, comparing to Cu-Zn-Al alloy. The presence of nickel, which slows diffusion processes can explain this behaviour, influenced by quenching rate and annealing time. We interpret the relaxation processes and the evolutions of  $M_s$  in term of atomic reordering (B2 and L21). These phenomena are so slow in Cu-Zn-Al-Ni alloys near room temperature that the equilibrium state of order cannot be reached.

### 1-INTRODUCTION

Cu-Zn-Al alloys exhibit within a certain range of composition a BCC disordered structure stable at high temperature which presents two successive ordering transitions during cooling. A B2 superlattice appears below a temperature  $T_{cB2}$  and orders to L21 superlattice at lower temperature (1) (2). Different heat treatments lead to partially ordered structures and the influence on martensitic transition temperature can be strong (3). Near room temperature, the non-equilibrium state obtained is able to evolve, leading to a modification of martensitic transition temperature (4) (5). This relaxation process results from exchanges of atoms among the different lattice sites via a vacancy mechanism. In this work, we compare the behaviour of two similar industrial alloys: a Cu-Zn-Al and a Cu-Zn-Al-Ni alloy. The influence of heat treatment on martensitic transformation temperature and further isothermal relaxation is investigated, putting in evidence the particular importance of quenching rate and annealing time in the case of Cu-Zn-Al-Ni alloy.

## 2-EXPERIMENTAL DETAILS

Two different alloy have been used in this work:

- a Cu-26,7Zn-4,1Al %wt industrial alloy with zirconium as refining element. The Ms temperature of this alloy is around - 45°C, as a function of the thermal treatment. The critical order disorder temperatures are  $T_{CB2} = 520^{\circ}\text{C}$  and  $T_{CL21} = 280^{\circ}\text{C}$ .

- a Cu-26,2Zn-3,7Al-1,1Ni %wt industrial alloy with zirconium as refining element. The Ms temperature of this alloy is around - 20°C, as a function of the thermal treatment. The critical order disorder temperatures are  $T_{CB2} = 520^{\circ}\text{C}$  and  $T_{CL21} = 280^{\circ}\text{C}$ .

Two different heat treatments have been performed in this study. They schematized figures 1 and two. The variable parameters of these treatments are the quenching conditions (water quenching or 150°C oil quenching) and the annealing time at 150°C.

After heat treatment, the martensitic transition temperature noted M50 (50 % of martensite formed) has been obtained either by detecting the acoustic emission generated during the transformation or using a Differential Scanning Calorimeter (Mettler). The results obtained by the 2 methods are good correlated. The measurements have been performed on samples 4 mm diameter and 2 mm thickness. It is important to note that measurement by acoustic emission takes only 4 minutes and allows to obtain with a good accuracy the evolution of M50 in the first stage of the relaxation process.

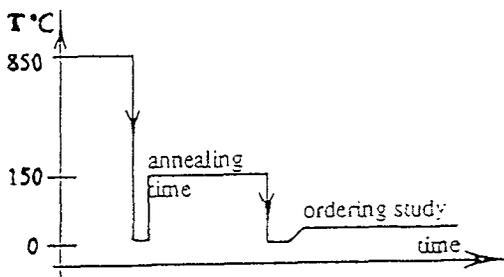


Figure 1 : Ta 150°C heat treatment

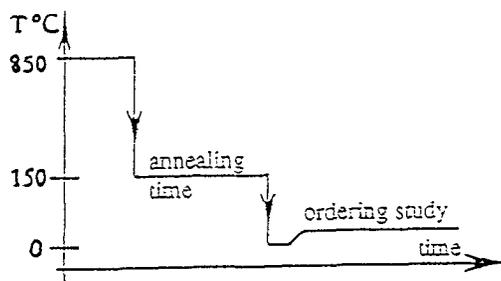


Figure 2 : Tq 150°C heat treatment

The relaxation process has been followed by measuring the power  $W$  dissipated from the revise it samples (dises 14 mm diameter, 1,5 mm thickness) during isothermal conditions (30°C in this work) using a high sensitivity differential conduction calorimeter (6).

## 3-RESULTS

Heat treatments involving annealing 10 minutes at 150°C after water quench (noted Ta150 10mn) and after 150°C oil quench (noted Tq150 10mn) have been performed on the Cu-Zn-Al and Cu-Zn-Al-Ni alloys.

In the case of Cu-Zn-Al alloy, the values of M50 temperature and its evolution at 30°C as a function of the time are reported on figure 3 which shows a very similar behaviour in the two cases. The M50 temperature exhibit globally a noticeable rapid increase at the beginning of the ageing time and a stable state is reached after around 48 hours (- 41°C). It is important to note that a decrease of the M50 temperature is observed at the early first stage (15-30 mn) of the evolution.

The results relative to the Cu-Zn-Al-Ni alloy and the beginning of the M50 evolutions at 30°C are reported an figure 4. In oppostion to Cu-Zn-Al alloy, the M50 temperature is strongly dependant of the quenching conditions. On the other hand, the aspect of the evolution curves are similar, exhibiting a slight decrease at the first stage of the phenomenom. It must be noticed that the evolutions of M50 in the case of the Cu-Zn-Al-Ni alloy are much slower companing to the Cu-Zn-Al one . The figure 5 show that a quasi stable state can be reached only in a few month. An other important result is that the difference in M50 temperature due to heat treatment (Ta150 10mn or Tq150 10mn) is conserved after ageing.

The influence of annealing time at 150 after 450°C oil quench has been investigated on Cu-Zn-Al-Ni alloy ( $T_q$  150° 2 mn, 10 mn, 30 mn, 3 h, 37 h) (figure 6). Annealing time doesn't have any influence on the initial M50 temperature (-31°C ± 1°C on all the measurements) but it is clear that increasing annealing time slowest further evolution. Measurements performed on the Cu-Zn-Al alloy show that the annealing time doesn't have any influence on the M50 temperature and the relaxation process.

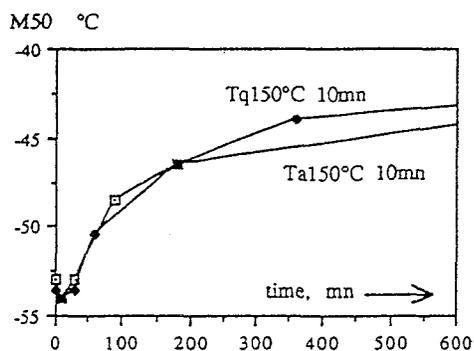


Figure 3 : M50 temperature evolution versus time at 30°C : CuZnAl alloy

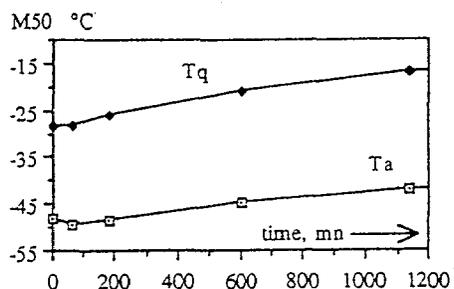


Figure 4 : M50 temperature evolution versus time at 30°C : CuZnAlNi alloy

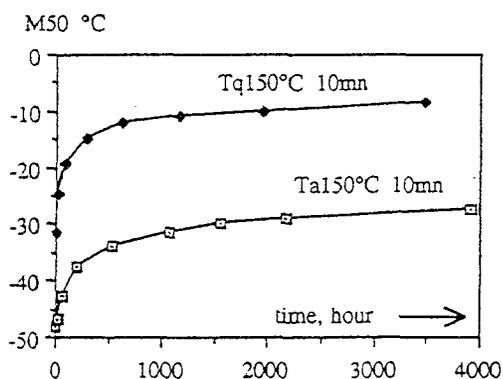


Figure 5 : M50 temperature evolution versus time in hour : CuZnAlNi alloy

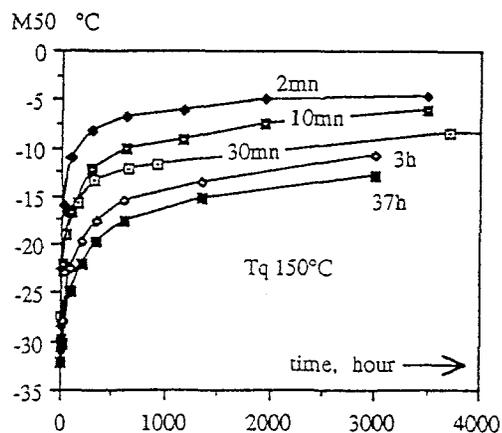


Figure 6 : M50 temperature evolution for different annealing time : CuZnAlNi alloy

Isothermal calorimetry investigations have been performed on both alloy to characterise the ordering kinetic, closely related to M50 evolutions.

The figure 7 presents to results of the released energy (integrated  $W$ ) as a function of the time at 30°C for the treatments Ta150 10 mn and Tq150 10 mn performed on the Cu-Zn-Al alloy. These two identical curves, show that the relaxation process doesn't follow a single exponential decay but a continuous slowing down. A method of defining an effective relaxation time for the whole process consists in taking the time  $t$  at which the product  $t \cdot W(t)$  exhibits the most pronounced maximum [5]. The relaxation time obtained after different heat treatments are summarized in table 1. These results show a very weak influence of the quenching rate and annealing time at 150°C on the characteristics of the relaxation process in the case of the Cu-Zn-Al alloy.

If one assume that  $t^{-1}$  is proportional to the initial equilibrium vacancy concentration at annealing temperature ( $T_1$ ) and to the vacancy mobility at calorimeter ageing temperature ( $T_2$ ), one can consider that  $t$  depends on  $T_1$  and  $T_2$  through an Arrhenius law [5]

$$t = A \exp(E_f/KT_1) \exp(E_m/KT_2)$$

$E_f$  and  $E_m$ , the effective formation and migration energies of vacancies for Cu-Zn-Al alloy have been reported to be respectively 0,43 eV and 0,76 eV [5].

The figure 8 presents the isothermal relaxation at 30° of the Cu-Zn-Al-Ni alloy (Ta150 10 mn, Tq150 10 mn). Table 1 summarize the results of others heat treatments. It is clear that in the case of Cu-ZnAlNi alloy, comparing to Cu-Zn-Al one, the relaxation process is strongly dependant of the quenching rate and the annealing time for this alloy.

Heat treatment	$\tau$ Cu-Zn-Al	$\tau$ Cu-Zn-Al-Ni
Tq150 10 mn	75 mn	210 mn
Tq150 1 h	75 mn	500 mn
Tq150 24 h	75 mn	600 mn
Ta150 10 mn	67 mn	900 mn
Ta150 1 h	71 mn	>1500 mn
Ta150 24h	50 mn	>1500 mn

Table 1

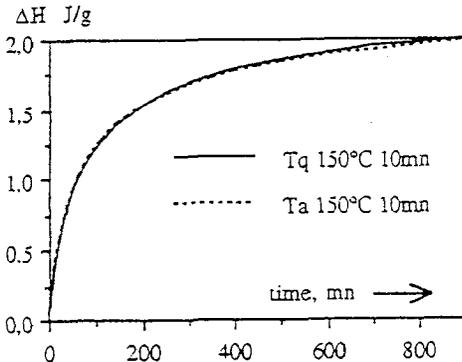


Figure 7 : Enthalpy evolution versus time at 30°C : CuZnAl alloy

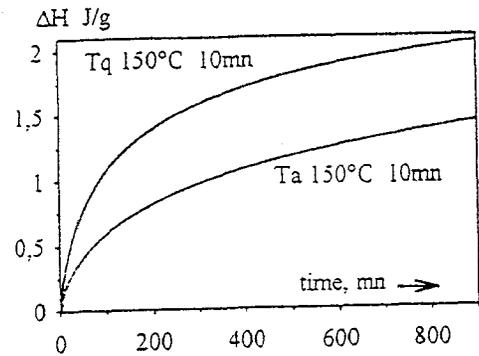


Figure 8 : Enthalpy evolution versus time at 30°C : CuZnAlNi alloy

#### 4. DISCUSSION AND CONCLUSION

In this paper, we have compared the isothermal relaxation process in a Cu-Zn-Al alloy and in a Cu-Zn-Al-Ni alloy.

Previous works on Cu-Zn-Al have shown that the relaxation process can be related to the reconstruction of the L21 order, further to the disorder frozen in the quench after annealing [4] [5]. This phenomenon involve exchange of atoms among the different lattice sites. The evolution of the vacancy concentrations and mobility during the evolution of the state of order is at the origin of the very complex relaxation law. However, it's important to note in this study two particular points : the decrease of M50 in the early stage of the relaxation process and the particular behaviour of Cu-Zn-Al-Ni alloy.

The abnormal behaviour of M50 evolution (decrease and increase) in the early stage of the relaxation process has already been observed by Planes [7]. Suzuki [8] and Castan [9] have reported the same behaviour on elastic constants. We think that this phenomenon could be related to two different ordering processes with opposed effects on M50, and thus, additive effects on isothermal calorimetric measurements. Since the long range ordered domains do not grow at room temperature [10] [11], these effects could be related to a rearranging of short range disorder. Inversion of B2 disordered Cu-Zn or Cu-Al atoms pairs could lead to a decrease of M50 temperature when inversion of L21 disordered Cu-Zn pairs involve an increase of M50

temperature [3]. It is possible that a small amount of residual B2 disorder is responsible of the small decrease of M50 at the early stage of the relaxation process.

The behaviour of Cu-Zn-Al-Ni appears to be different comparing to the Cu-Zn-Al. The continuous evolution of relaxation time as a function of the thermal treatment parameters indicates that the alloy doesn't reach any equilibrium state during annealing. Since the annealing time doesn't affect the initial value of M50 but slows the evolution kinetic of the alloy, it is possible that the state of order is reached rapidly at 150°C when the vacancy concentration equilibrium is continuously decreasing. This particular behaviour prevents the possible calculation of activation energies for the formation and migration of vacancies. Relaxation kinetics slower and lower M50 temperature in the case of water quench are certainly due to the presence of quenching defects and small ordered domains [12]. The study of this behaviour imposes to consider a contribution of the driving force of ordering process, the vacancy concentration and their mobility. Each of these parameters evolve with time at constant temperature.

The fact that the Cu-Zn-Al-Ni doesn't reach any equilibrium state during thermal treatment and present a relaxation kinetic very slow which is continuing on several days or a few months shows that diffusion processes in this alloy are very slow. The Nickel element, which slow diffusion coefficients (Mwanba) [13] is probably the main reason of this particular behaviour.

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