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EVOLUTION OF THE MARTENSITIC TRANSFORMATION BY AGEING IN A Cu-Al-Ni SHAPE MEMORY ALLOY

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Abstract - Ageing phenomena in the martensitic phase β'_1 of Cu-Al-Ni base shape memory alloys (SMAs) are rather slow; the visible outcome is a progressive evolution of the characteristics of the martensitic ⇔ parent phase transformation. During thermal cycling, these phenomena induce only a small stabilization of the martensitic phase. However, the modification in the characteristics of the transformation on heating and cooling after ageing in the β_1 phase are more complex. From DSC measurements, it was shown that a precipitation process occurs between 220 and 370 °C. When samples initially in the quenched state are cycled, several evolutions during ageing change the shape memory capability by a more or less important degradation of the thermoelastic character of the martensitic transformation.

Résumé - Evolution de la transformation martensitique au cour du vieillissement dans un alliage à mémoire de forme à base de Cu - Al – Ni. Le fait d'imposer un vieillissement en phase martensitique β'_1 à des alliages à mémoire de forme (AMF) du type Cu-Al-Ni se traduit par une évolution progressive des caractéristiques de la transformation martensite ⇔ phase mère. Les phénomènes développés pendant le vieillissement sont à l'origine d'une stabilisation très limitée de la martensite. Par contre, la modification des caractéristiques des transformations au chauffage et au refroidissement est complexe lorsque l'on procède à des vieillissements affectant la phase mère β_1. En particulier, l'étude par DSC a permis de montrer qu'un processus de précipitation se développe dans le domaine des températures comprises entre 220 et 370 °C. En imposant un cycle thermique à des échantillons initialement à l'état trempé, nous avons pu distinguer plusieurs stades successifs de vieillissement. Les différentes évolutions structurales intervenant ont alors pour conséquence de modifier l'effet mémoire, en altérant de façon plus ou moins importante le caractère thermoélastique de la transformation martensitique.

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1. INTRODUCTION

The various studies performed on several copper based SMAs (Cu-Zn-Al) have shown that ageing in the martensite phase can induce a stabilization of this martensite so that this phase will never transform on heating even at high temperature (above the Af point) [1-5]. In order to avoid this stabilization phenomenon, some authors recommend a short tempering just after quenching [6]. Although the stabilization phenomena are less pronounced in Cu-Al-Ni SMAs, the same treatment is sometimes applied.

Different authors have studied the ageing behaviour of copper base SMAs, using various methods (differential scanning calorimetry D.S.C, electrical resistivity, thermoelectric power, ...) [3,7,8,9]. Nevertheless, the effect of ageing on ($\beta'_1 \leftrightarrow \beta_1$) transformations (either on heating or on cooling) are not well understood.

An ageing treatment applied to the non equilibrium structure β_1 in Cu-Al-Ni SMAs is likely to provoke gradual modifications in the thermoelastic transformation characteristics ($\beta'_1 \leftrightarrow \beta_1$). If a non equilibrium structure is heated at a sufficiently high temperature (to allow diffusion phenomena even over short distances), and maintained during a sufficient time, a precipitation of equilibrium or intermediate phases occurs.

In the case of the Cu-Al-Ni SMAs, ageing at temperatures higher than the Af point leads to the formation of phases with a high aluminium content (γ_2 and β'_2 of compositions Cu_9Al_4 and NiAl, respectively) [7,10,11]. Other authors agree that the atomic reordering during ageing in the parent phase is responsible for a change in the martensitic transformation behaviour, and causes the temperature characteristics to shift upwards [8,9]. Wei et al. [9] assert that in advanced states of ageing, the fall in the martensitic transformation temperature is associated with bainite formation.

In the present work, a Cu-Al-Ni SMA with 13.1 Al, 4 Ni and 0.015 B contents (wt.%) was used. In this alloy the transformation temperatures are relatively high (Ms = 155 °C, Mf = 135 °C, As = 162 °C, and Af = 175 °C). *Figure 1* shows a DSC diagram recorded during a slow heating (2 °C/min), from ambient temperature to the single phase β domain [12].

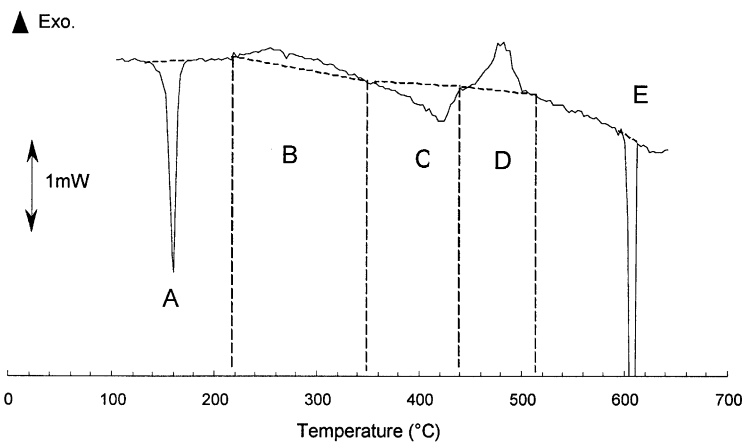

Figure 1. DSC diagram obtained during a slow heating (Vh = 2 °C/min) of the quenched structure.

Five evolutions are observed:
A: martensite transformation on heating ($\beta'_1 \rightarrow \beta_1$),
B: first precipitation of intermediate phases,
C: partial redissolution of the coherent precipitates,
D: rapid decomposition of the β_1 phase to equilibrium phases ($\alpha + \gamma_2$),
E: transformation of ($\alpha + \gamma_2$) into β phase, stable at high temperature.

According to Singh et al. [10], the remaining γ_2 phase decomposes to a β solid solution and β'_2 phase at temperatures above 620 °C.

2. EXPERIMENTAL METHODS

The working life of the SMAs is directly dependent on their behaviour on ageing. The progressive loss of the memory effect might have serious consequences, especially if it is important to know perfectly the temperature range in which the ageing kinetics becomes too fast. For this type of alloy, process B above is mainly responsible for the ageing phenomenon. In fact, the treatment temperature θa was fixed either early in the B domain (i.e. θa = 225 °C), or between 250 and 350 °C. In the case of slow ageing kinetics, the sample was maintained in a tubular furnace (θa = 225 °C); after each treatment, the sample was cycled between θa and room temperature in a DSC apparatus. When ageing kinetics are faster, the samples were directly cycled in the DSC with a 10 min isothermal holding at the maximum temperature.

3. RESULTS AND DISCUSSION

3.1. Ageing at 225 °C

From *figures 2(a)* and *2(b),* four successive stages of ageing can be distinguished.

Stage I: It concerns the first 200 minutes of ageing. During this time, the temperatures for the $\beta_1 \rightarrow \beta'_1$ transformation and the inverse one (Ms, Mf, As, Af and the temperatures Tm and Ta in the top of the DSC peaks) remain approximately constant. We also noticed that the enthalpy change, as well as the width, hysteresis and intensity of the peaks (Im and Ia) on the DSC diagrams remain unchanged. Therefore, the shape memory properties are approximately stable during this stage.

Stage II: This stage is longer than stage I, that means between 200 and 4000 min. During this stage, changes in all characteristics are approximately linear. However the variation of As and Af points are more important. This increases slightly the hysteresis between transformations on heating and cooling: the hysteresis varies from about 17 °C at the end of stage I to about 22 °C at the end of stage II. We also observed a noticeable change in the peak shapes during the transformation on heating. Indeed, the intensity of peak Ia (associated to the $\beta'_1 \rightarrow \beta_1$ transformation) increased gradually from 7.7 mW (after 200 min ageing) to 9.2 mW (after 4000 min at 225 °C). The intensity of peak (Im) for the martensitic transformation is less important. Moreover, the enthalpy change for the $\beta'_1 \Leftrightarrow \beta_1$ transformations remains more or less approximately constant.

Stage III: This stage is mainly characterized by a steady decrease in the peak heights as well as in the enthalpy variation during transformations on cooling and/or heating. At the same time, we observed that other characteristics of the $\beta'_1 \rightarrow \beta_1$ transformation continue to develop: in particular, the peaks became broader and the hysteresis becomes more important. We also noticed that As and Af increase more rapidly than Ms and Mf. The Af point reaches a maximum value (216 °C), and the other characteristic points have a strong tendency to decrease as ageing is done near the end of this stage. At the same time, the shape of the DSC transformation peak on heating shows some irregularities on its left side (see black arrows on *figures 3 and 5*), similar to a burst phenomenon.

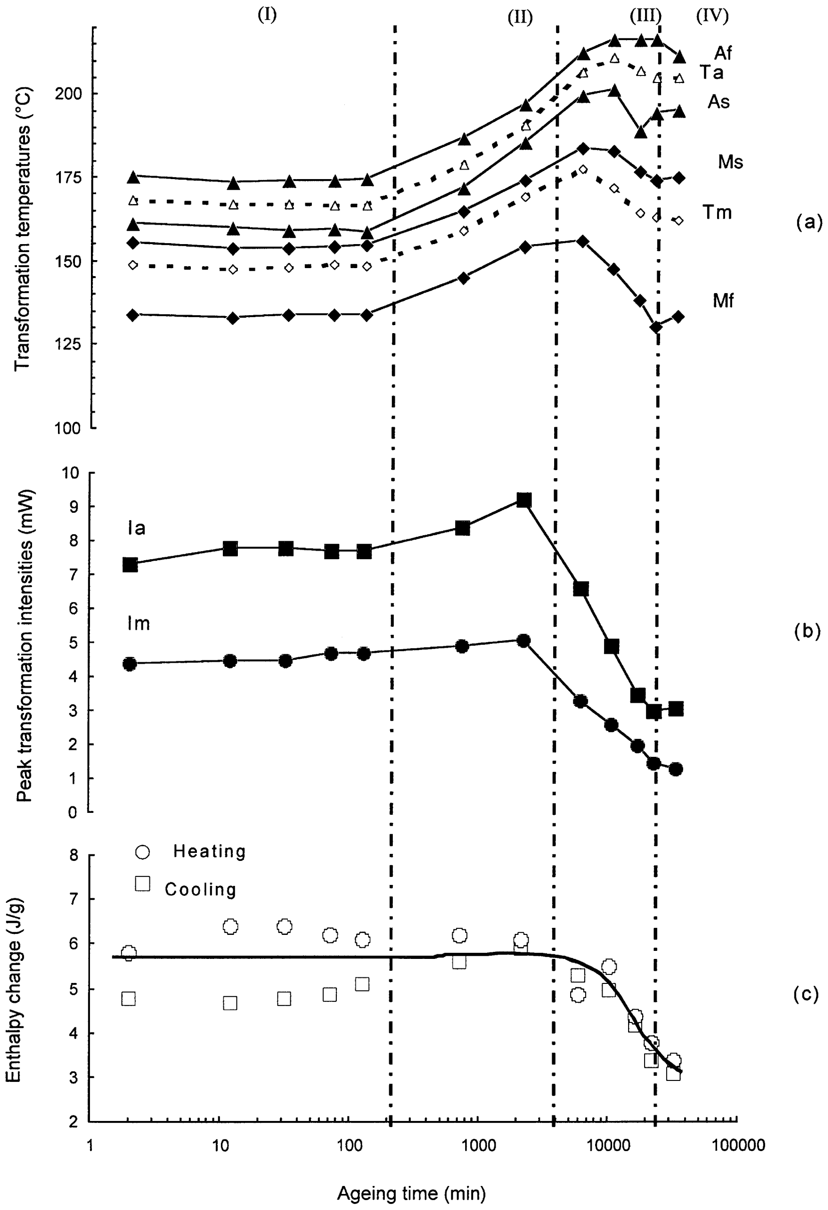

Figure 2. Evolution of the martensitic and inverse transformation characteristics after ageing at 225 °C**:** (a) evolution of the temperature characteristics, (b) evolution of the peak transformation intensities, (c) evolution of the enthalpy change.

Stage IV: This stage is easily displayed by the peak intensities (see *figure 2* (b)). Iı during this last stage, the peak heights have a tendency to keep their minimum values (Im = 1. and Ia = 3.5 mW). Moreover, stage IV starts when the burst phenomenon disappears. Durir stage one observed:

- a stabilization of the hysteresis (42 °C),
- a stabilization of the peak width.

Even during this last stage of ageing, owing to the formation of equilibrium phases (' β'$_2$) in precipitate form, the thermoelastic behaviour of the β'$_1$ ⇔ β$_1$ transformation is c affected. However, on account of the precipitation processes which are rather brief ε temperature, there is a volume fraction of the parent phase which is still transformed to martı even after more than 30 days at 225 °C.

3.2. Ageing at 300 °C

According to the characteristics of the previous martensitic transformation and of the iı one illustrated on *figure 3*, we noticed that their behaviour show some similarities with tł observed on ageing at 225 °C. However, the first stage is missing while the transforn characteristics are modified from the beginning on the first heating to 300 °C. Moreove different stages of ageing observed are shorter (*figure 4*).

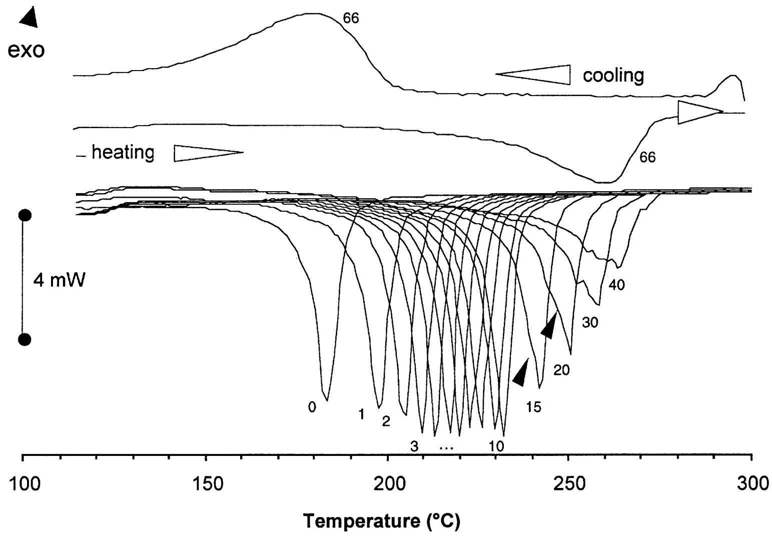

Figure 3. DSC diagrams of the transformations on heating and cooling, showing the evolution of the peak shape during thermal cycling with a keeping of 10 min at high temperature (300°C). At the ith cycle corresponds a cumulated time of i x 10 min, except for cycle 0 which corresponds to a treatment without keeping at high temperature (cycle number i is indicated for each curve).

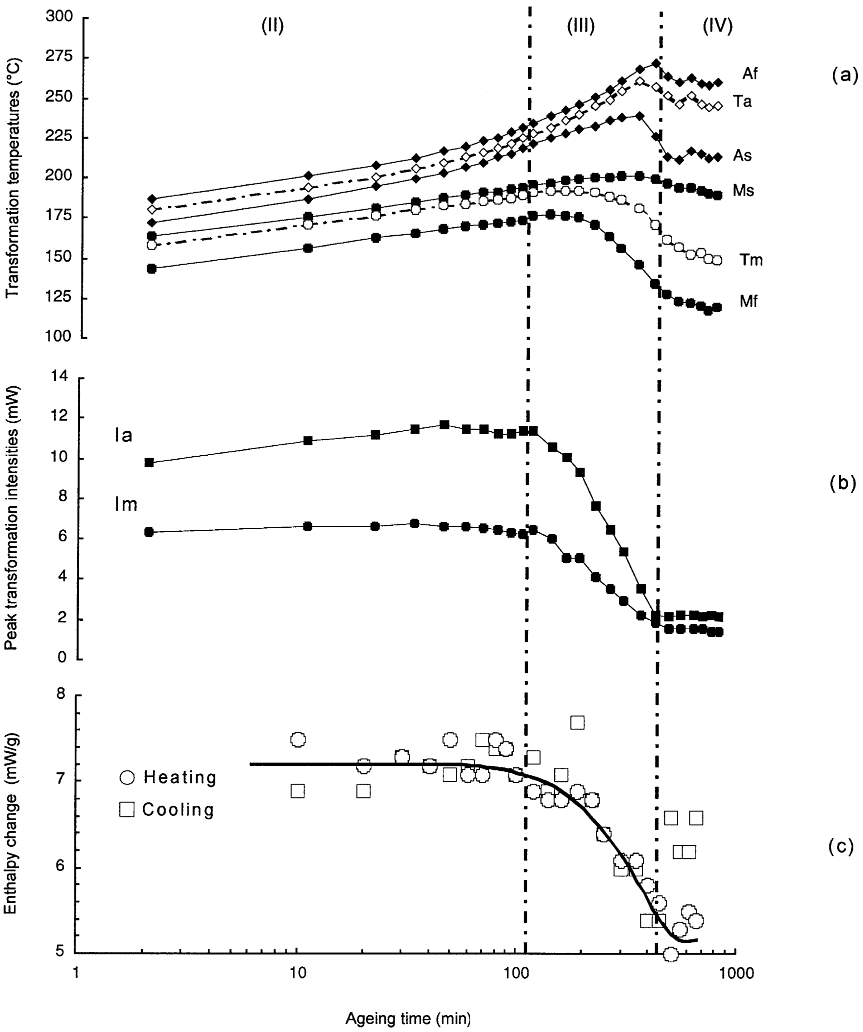

Figure 4. Evolution of the martensitic and inverse transformation characteristics after ageing at 300 °C: (a) evolution of the temperature characteristics, (b) evolution of the peak transformation intensities, (c) evolution of the enthalpy variation.

Stage II: It develops during the 100 first minutes of ageing (cumulated isothermal treatment of 10 min at 300 °C for each cycle). Its characteristics are as the following:

- the peak height (Ia) for the $\beta'_1 \rightarrow \beta_1$ transformation increases slightly (from 10 to 11.5 mW), while that of the $\beta_1 \rightarrow \beta'_1$ peak remains sensibly constant (Im = 7 mW),
- the hysteresis increases slightly with the ageing time,
- the enthalpies of transformation on heating and cooling remain approximately constant.

Stage III: After a 100 min holding at 300 °C (10 consecutive cycles), the peak corresponding to the transformation on heating presents a small anomaly indicating a transformation by a burst phenomenon (see *figure 3*). Furthermore, this phenomenon is not observed on the following transformation. On subsequent cycles, the burst phenomenon emerges on the left side of the peak; then, around the middle of this stage, it affects the whole peak (see 30th and 40th cycle peaks on heating). At the end of this stage, this phenomenon disappears progressively on the right side of the peak. As it was observed in the case of ageing at 225 °C, this stage is also characterized by a progressive decrease in the DSC peak heights. Also, the changes in the characteristic temperatures (Ms, Mf, As, Af, …) are similar to those observed during ageing at 225 °C.

Stage IV: This stage of ageing starts when the burst transformation phenomenon has vanished completely. In that case, the transformation points exhibit a clear tendency to stabilize. The heights of the DSC peaks remain virtually unchanged, while their shapes are rather squashed. During this ultimate stage of ageing, we observed that the thermal hysteresis between the transformations (see peaks on the 66th cycle in *figure 3*) is very important (about 90 °C). However, the complete decomposition of the β_1 phase into the equilibrium phases was not reached even after 1150 h of holding at 300 °C

3.3. Ageing at 350 °C

DSC diagrams (*figure 5*) and curves representing the change in transformation characteristics v.s. cumulated ageing time at 350 °C (*figure 6*), show the same stages as before (that is when ageing temperature is 300 °C). Furthermore, due to the rapid ageing kinetics at this temperature, these stages are relatively short.

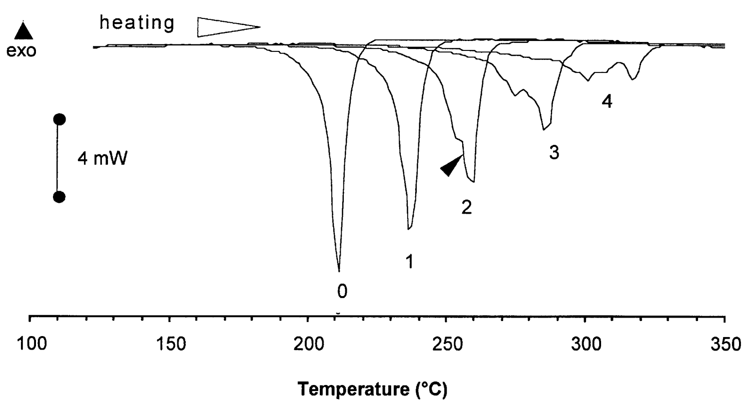

Figure 5. DSC diagrams of the transformations on heating and cooling, showing the evolution of the peak shape during a thermal cycling with a holding of 10 min at high temperature (350°C). The ith cycle corresponds to a cumulated time of i x 10 min, except cycle 0 which corresponds to a treatment without holding at high temperature.

Stage II: In comparison with ageing behaviours at lower temperatures, stage II is effectively shorter and, in fact, the burst phenomenon appears already on the heating peak of cycle 2.

Stage III: This stage of ageing starts immediately after cycle 1, and finishes on cycle 5, when the burst disappears. This last phenomenon is rather similar to the one observed previously, but it appears in a shorter time. It was also noticed:

- a decrease in amplitude of the peaks, associated with an important broadening,
- a regular decrease in enthalpy.

The maximum value of the As temperature was observed at the end of this stage of ageing (As = 325 °C).

Stage IV: During this last stage of ageing, the characteristic temperatures of the $\beta'_1 \Leftrightarrow \beta_1$ transformation evolve practically in the same manner as observed on ageing at lower temperatures. We also noticed that the complete decomposition of the parent phase (β_1) is not observed, even after a cumulative holding time of about 50 h at 350 °C.

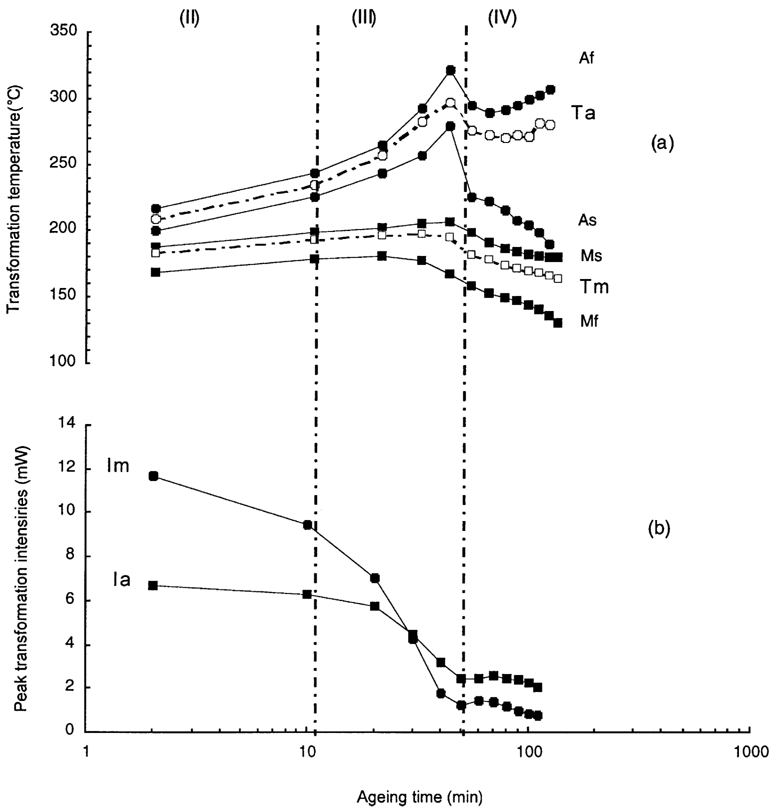

Figure 6. Evolution of the martensitic and inverse transformation characteristics after ageing at 350 °C: (a) evolution of the temperature characteristics, (b) evolution of the peak transformation intensities.

4. CONCLUSION

During the operation of an SMA, the degradation of the memory effect is the result of the modification of the martensitic transformation due to the precipitation of metastable and/or equilibrium phases during the treatments at temperatures above Af. This phenomenon is magnified when the ageing temperature is in the range corresponding to evolution process B (precipitation of intermediate phases). The basic points of the ageing behaviour in Cu - Al - Ni SMAs may be summarized as follows:

a) The precipitation kinetics at a temperature just above Af is very slow: a treatment of 60 h at 225 °C produces only minor modifications in the martensite transformation. On the contrary, some minutes of ageing at a higher temperature (300 °C) are sufficient to reach a noticeable change in the β_1 parent phase structure.
b) In most cases, four successive stages of ageing can be observed. Theses stages can be distinguished either by the shape of DSC peaks, or by the other transformation characteristics (Ms, Mf, As, Af, IM and IA).
c) The respective time durations of the different ageing stages are shorter when the maximum treatment temperature is increased. Indeed, the first stage is not observed when the maximum temperature is fixed at 300°C or more. However, stage IV is not finished at the end of all applied treatments.
d) The highest Af point was observed during stage III. However, the Af point remains always lower tante temperature of ageing, whatever the duration of treatments.

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