A Two-Stage Martensite Transformation in a Cu-13.99 mass% Al-3.5 mass% Ni Alloy

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The reverse martensite transformation of an as-quenched Cu-Al-Ni shape memory alloy presents two separate stages which are studied by means of calorimetry. The first stage, corresponding to the lower temperatures, presents a thermal hysteresis of about 10 K, a continuous behaviour of the energy dissipation and a very low acoustic emission. The second stage, at higher temperatures, presents a thermal hysteresis of about 40 K, a rather jerky character in the energy dissipation and a higher level of acoustic emission. The first stage progressively disappears and the transformation temperatures increase when the alloy is aged at 473 K or 573 K but the difference in temperatures between the two stages, of about 25 degrees, remains constant. An analysis by SEM of the microstructure during the transformation, in accordance with the above-mentioned features, shows that the $\beta'$- and $\gamma'$-phases coexist in the martensite. The first stage is a $\beta' \rightarrow \beta$ transformation, while the second stage is a $\gamma' \rightarrow \beta$. The occurrence of the $\beta'$ martensite is assisted by internal strain energy created during the direct transformation. The relative amount of $\gamma'$-martensite increases by ageing at 473 K or 573 K.

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II. Experimental

Polycrystalline samples (6.1 mm in diameter, 0.25 mm in thickness) of a Cu-Al-Ni alloy with a nominal composition Cu-13.99 Al-3.5 Ni mass% have been used. The original ingot was obtained by melting weighted amounts of the initial components (99.99% purity) in an induction furnace. Cylindrical bars were obtained from the 8 kg ingot by hot-extrusion at 1173 K. The samples were cut from the extruded bars using a diamond blade. Finally they were annealed at 1173 K for ten minutes and quenched in a mixture of ice and water (first quench). When studying the transformation evolution with ageing time, the samples were transferred, after quenching, into a liquid salt-bath maintained at 473 K or 573 K, kept there for a predetermined ageing time and then quenched again in a mixture of ice and water (second quench).

The experimental system used in the calorimetric and acoustic emission measurements has already been described elsewhere.  

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III. Experimental Results

Figure 1 shows a typical picture for the thermal power released during the direct and the reverse transformation just after a first quench. The reverse transformation shows clearly two different separated stages A and B, which are not visible for the direct one. This is even clearer in Fig. 2, where the relative accumulated enthalpies are drawn as a function of temperature. However, an experiment was also performed in which, once the direct transformation was completed, the sample was heated up to the final temperature of the low temperature stage \((A_f)\) and then cooled back until the direct transformation was again completed. The results of this experiment are presented in Fig. 3, which shows that the low temperature stage is well defined also on cooling, with a hysteresis of about 10 degrees, while the high temperature stage presented (Fig. 2) a transformation hysteresis of about 40 degrees.

The main features of the described two-stage reverse transformation are the following:

![Graph](image)

Fig. 1 Typical picture for the thermal power released during the direct and reverse transformation after a first quench for a Cu-13.99 mass% Al-3.5 mass% Ni alloy. The two stages observed during the reverse transformation, together with the characteristic temperatures of each stage, are also shown.
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(1) The starting temperatures of both stages ($A_{s1}$ and $A_{s2}$) are always separated by about 25 degrees, independently of any previous thermal treatment;

(2) The low temperature stage has an essentially continuous behaviour, while the high temperature stage shows sharp discontinuous peaks superimposed on a continuous background;

(3) During the low temperature stage a small amount of acoustic emission is detected. The ratio for the accumulated number of counts between stages A (low temperature) and B (high temperature) is always much smaller than the corresponding ratio for other transformation magnitudes such as the enthalpy or en-

Fig. 2 Relative accumulated enthalpy for the direct and reverse transformation pictured in Fig. 1 as a function of temperature.

Fig. 3 Relative accumulated enthalpy versus temperature for stage A during heating till the final temperature $A_{f1}$ and during cooling until the direct transformation is again completed. The dotted line represents a typical evolution of the enthalpy if the heating is not stopped at $A_{f1}$.
tropy changes;
(4) The interval between the two stages presents (at least in the first cycle after quenching) some small peaks which ensure that the transformation does not stop between both stages.

Table 1 presents the characteristic magnitudes of the reverse transformation after a first cooling following a direct quench for two samples of the same alloy. The results for sample 1 correspond to the transformation pictured in Fig. 1. The values of $\Delta H$ and $\Delta S$ given in Table 1 have been computed from the heat measured in the different stages and divided by the whole mass of the sample. Consequently, they cannot be considered as enthalpy and entropy changes characterizing the transformations associated to stages A and B, in every one of which the sample does only transform partially.

To investigate the origin of the double transformation, the evolution of the reverse transformation after ageing the sample for different times at 473 K or 573 K has also been studied. The results obtained from these series of experiments are summarized in Fig. 4:

(i) The most noticeable feature (Fig. 4-B) is the progressive disappearance of the low temperature stage (stage A) with increasing ageing time. The disappearance is completed after 45 s at 573 K, while it takes more than 7.2 ks (120 min) at 473 K. This suggests that a thermally activated process is responsible for the disappearance of the double stage.

(ii) The transformation temperatures (Fig. 4-C) shift with increasing ageing time, but at very different rates for the two ageing temperatures. At a certain time the rate of evolution of

| Stage | Sample 1 | Sample 2 |
|-------|----------|----------|
| $A_1$ (K) | 251.8 | 276.6 | 250.6 | 276.9 |
| $A_2$ (K) | 268.1 | 307.5 | 269.2 | 308.2 |
| $\Delta H$ (J/mol) | 108.4 | 181.2 | 105.4 | 164.9 |
| $\Delta S$ (J/mol K) | 0.414 | 0.635 | 0.402 | 0.577 |

Fig. 4 Diagram showing the influence of ageing time at two ageing temperatures ((x) 473 K, (o) 573 K) on the total enthalpy change (A), the relative enthalpy change of stage A referred to the total enthalpy change (B), and the starting temperatures of stages A and B (C).
ing temperature.

(iii) The total changes in enthalpy (and entropy) for the reverse transformation, as calculated by adding the contribution of both stages, also vary with ageing time (Fig. 4-A). After an initial decrease, the enthalpy increases to reach a nearly constant value after 15 s of ageing at 573 K. However, at 473 K a constant value is not reached even after 120 minutes of ageing, although for this ageing temperature an equivalent behaviour is expected at longer ageing times.

It has been found that ageing also modifies the forward transformation temperatures and the thermal hysteresis of the two stages. The corresponding results are shown in Fig. 5. $M_{s2}$ and $M_{f1}$ refer to the start and the final temperature of thermal activity, which always shows a single calorimetric peak.

(i) $M_{s2}$ increases monotonically with increasing ageing time, at different rates for the two ageing temperatures (Fig. 5-A).

(ii) For the two ageing temperatures, the difference $A_{s2} - M_{s2}$ (representing the thermal hysteresis for the transformation stage B) decreases with ageing at a slightly higher rate than $A_{s1} - M_{f1}$ (representing the thermal hysteresis for stage A). This is shown in Fig. 5-B and Fig. 5-C. The scatter in the experimental points is rather large; this is due to large uncertainties in the determination of $A_{s2}$ and $M_{f1}$ from the calorimetric thermogram. Nevertheless, the behaviour represented in Fig. 5-B has been confirmed independently by resistivity measurements on the same alloy aged at 453 K.

Additionally, in order to make clear the origin of the two stages, a series of pictures in the SEM were taken in the course of a reverse transformation after cooling from a first quench. The weak contrast of the pictures (Fig. 6) is associated with a very weak surface relief in the transformation. The observations in the SEM show that the martensitic phase involves two kinds of structures: One of them consists of big plates with a typical $\gamma'$ microstructure, while the other consists of clustered zones with very fine needles of a $\beta'$ microstructure. On heating in the range between 233 and 273 K, which corresponds to the low temperature stage (stage A) the small and fine needles move and shrink while the other regions remain unaffected. This process finishes
around 273 K. The big plates surround now small regions of the sample where the surface relief has disappeared. Further heating does not produce any observable change in the whole microstructure until a temperature around 280 K is reached. Then, in the range between 280 K and room temperature, which corresponds to the high temperature stage, (stage B) the large $\gamma'_1$ martensite plates are those which quickly shrink, leading back to the parent $\beta_1$ phase. A sample aged for 300 s (5 min) at 573 K was also observed in the course of a reverse transformation; the polishing had been performed in the $\beta$-phase before the ageing treatment. In this case, not only the clustered zones of small needles cannot be observed, but the surface relief moves back and disappears continuously during heating, without any observable interruption.

### IV. Discussion

From the preceding results we conclude that two kinds of transformation are operative: Firstly a $\beta_1 \rightarrow \gamma'_1$ transformation, in the temperature region of stage B, which exhibits a characteristic "jerky" behaviour and gives rise to a morphology of large and thick martensite plates; secondly, a $\beta_1 \rightarrow \beta'_1$ transformation, in the low temperature region of stage A, which shows a more thermoelastic behaviour and gives rise to a microstructure of clustered zones of very fine needles in the remaining parent regions surrounded by the $\gamma'_1$ plates.

This conclusion is consistent with and based on the results discussed in ref. (4):

(i) A "jerky" behaviour is typical for a $\beta_1 \rightarrow \gamma'_1$ transformation.

(ii) The thermal hysteresis for $\beta_1 \rightarrow \gamma'_1$ is
larger than for $\beta_i \rightarrow \beta'_i$. The difference in hysteresis explains also why in the direct transformation the two stages are not distinguishable from each other; experimental evidence has been given, however, for the existence of two different stages of transformation also on cooling.

(iii) The difference in the acoustic emission recorded during the reverse transformation between the two stages is also related with the difference in thermoelastic character between $\beta_i \rightarrow \beta'_i$ and $\beta_i \rightarrow \gamma'_i$ transformations.

As mentioned in the introduction, the possibility of obtaining different kinds of martensite for a Cu–Al–Ni alloy with a given composition has been pointed out by several authors\(^{(1)(2)}\). Similar results for a Au–Cd alloy are also known\(^{(5)}\). In all these cases, the mechanism is a successive martensite to martensite transformation, induced by increasing the amount of externally applied uniaxial stress. In our case two martensitic transformations, $\beta_i \rightarrow \gamma'_i$ and $\beta_i \rightarrow \beta'_i$, are thermally induced sequentially in different regions of the specimen. The resulting structure is formed of two different martensite phases, as observed in the SEM.

1. Origin of the two-stage transformation

From a thermodynamical point of view, the existence of two transformations leading to two martensite structures in the same specimen is explained in Fig. 7.

The lines corresponding to $M_s$, $A_s$ and the equilibrium temperature $T_0$ are plotted for $\beta_i \rightarrow \gamma'_i$ and $\beta_i \rightarrow \beta'_i$ transformations. In the composition region of the alloy under investigation thermally-induced $\gamma'_i$ and $\beta'_i$ martensite nucleate nearly at the same temperature and hence the two $M_s$ temperatures are almost coincident for $\sigma = 0$. The difference in hysteresis between both transformations has also been considered; the larger hysteresis for the $\beta_i \rightarrow \gamma'_i$ transformation places $T_0(\gamma'_i)$ and $A_s(\gamma'_i)$ for thermal martensite ($\sigma = 0$) at higher temperatures than the corresponding $T_0(\beta'_i)$ and $A_s(\beta'_i)$. The difference in the slopes $-\Delta S_p^b-M/\Delta e_p^b-M$. $V_m$ is due to a double contribution: On one side the entropy changes $-\Delta S_\beta^b-\gamma'_i > -\Delta S_\beta^b-\beta'_i$, and on the other side the transformational shape changes $\Delta e_\beta^b-\gamma'_i < \Delta e_\beta^b-\beta'_i$, while the mean molar volume $V_m$ can be taken similar for both phases.

On cooling, thermal $\gamma'_i$ and $\beta'_i$ grow practically at the same temperature in different regions of the specimen. These regions can be considered as mutually non-interacting in a first approximation, due to the self-accommodating growth of the martensitic plates. Every self-accommodating region behaves almost independently of the other regions. Then, the diagram shows that during the reverse transformation on heating the $\beta'_i$ phase disappears first, as $A_s(\beta'_i)$ is reached first, and is followed by the disappearance of $\gamma'_i$, in other regions, at a higher temperature.

Actually the different regions in the specimen cannot be considered as completely non-interacting. The self-accommodating growth of different martensite variants indeed minimizes the effects of the transformational shape change. But volume changes associated with the transformation and remaining non-accommodated shape changes result in a continuous increase of the total internal elastic strain energy stored in the specimen.

At $M_s(\gamma'_i)$ the matrix is in a strain-free situation. As the first $\gamma'_i$ plates nucleate and begin to grow, strain energy is progressively stored in the matrix and opposes further nucleation or growth. Hence, continuous cooling below $M_s(\gamma'_i)$ is required to overcome the increasing resistive forces and to proceed with the transformation. During this continuous cooling, a temperature lower than $M_s(\beta'_i)$ (for
is reached, at which the $\beta_1 \rightarrow \gamma'_i$ transformation is arrested and the remaining parent phase, locally strained by the $\gamma'_i$ martensite already formed, transforms to $\beta'_1$ on cooling. The increase in total internal strain energy due to a $\beta_1 \rightarrow \beta'_1$ transformation is smaller than for a $\beta_1 \rightarrow \gamma'_i$ transformation. This is due to several factors, mainly the difference in crystallography between the two transformations, and the different behaviours of the elastic constants. Hence, at a certain moment the formation of $\beta'_1$ is more favourable than that of $\gamma'_i$, as a self-accommodating $\beta_1 \rightarrow \beta'_1$ transformation in the regions surrounded by strained $\gamma'_i$ plates helps more in locally relaxing the elastic strain field and increases less the total internal strain energy.

During the reverse transformation, on heating, things will occur in reverse sequence due to the local character of the thermoelastic equilibrium achieved at each temperature, in agreement with our observations. The difference in thermal hysteresis between the two transformations will cause that, once all $\beta'_1$ has retransformed into the parent phase, some overheating is necessary to begin the retransformation of $\gamma'_i$, as discussed before.

2. Influence of ageing

The influence of ageing on the shape of the hysteresis cycles is represented schematically in Fig. 8 together with the evolution of the transformation temperatures relevant to our discussion. A temperature $T=M_{s1}=M_{f2}$ is defined as the temperature (during the forward transformation) at which the relative amount $x$ of martensite in the specimen is the same than at $A_{s2}$, beginning of stage B, during the reverse one. It represents the temperature at which the formation of $\gamma'_i$ martensite is arrested during cooling and $\beta'_1$ martensite begins to be formed. The sequence of ageing times has been chosen in such a way that the evolution of the different temperatures is simply represented by straight lines. Aside from this simplification, the representation shows how the different experimental features observed during ageing are mutually compatible:

(i) Stage A progressively disappears and all the temperatures increase with increasing ageing time.

(ii) $A_{s2}$ is always separated from $A_{s1}$ by the same temperature interval; hence the two lines are parallel.

(iii) $M_{s2}$ increases at a higher rate than any other temperature.

(iv) The forward transformation proceeds without interruption during cooling. Correspondingly $M_{s1}$ does not increase as much as $M_{s2}$ because the corresponding $x$ also increases during ageing.

(v) $M_{f1}$ increases at a slightly higher rate than $A_{s1}$; therefore the hysteresis $(A_{s1}-M_{f1})$ of stage A decreases with ageing.

(vi) The hysteresis $(A_{f2}-M_{s2})$ associated with stage B decreases with ageing at a higher rate than the hysteresis of stage A.

Two different mechanisms can be operative during ageing an as-quenched Cu-Al-Ni alloy, as reported in the literature:

(i) A change in alloy composition due to precipitation of the $\gamma_2$ phase(8)-(10).

If precipitation of the stable $\gamma_2$ phase takes place, the parent matrix contains less Al and
the transformation temperatures increase during ageing. But at the same time this favours the formation of the \(\beta'_1\) phase (in the Al-poor zone of the Cu-Al phase diagram\(^{(11)}\)), which is contradictory to our observations. Actually we have not observed any precipitation in the course of our ageing experiments, and consequently this mechanism must be disregarded here.

(ii) Reordering of the parent phase.

The DO\(_3\) structure of the parent phase is not completely ordered after the first quench. In a Cu–Al–Ni alloy, ageing increases the DO\(_3\) order\(^{(12)}\) or changes the structure into an ordered Heusler one\(^{(8)}\). In any of the two cases the transformation temperatures increase.

Our results show that \(M_{s2}\) associated with a \(\beta_1-\gamma'_1\) transformation (stage B) increases during ageing at a higher rate than \(M_{s1}\), associated with a \(\beta_1-\beta'_1\) transformation (stage A); and that, during ageing, the critical driving force required to nucleate the \(\gamma'_1\) martensite, as represented by the thermal hysteresis of stage B, decreases more than the one required to nucleate the \(\beta'_1\) martensite, related to the thermal hysteresis of stage A. Correspondingly, the \(\beta_1-\gamma'_1\) transformation is progressively favoured and a smaller transformed volume of \(\beta'_1\) is formed.

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