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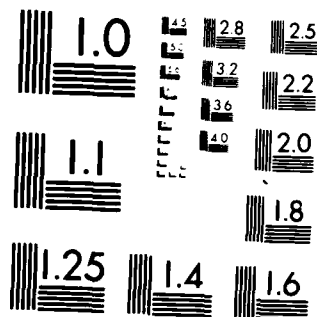
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ABSTRACT

The effect of thermal cycling between the M_f - A_f on the thermal hysteresis, temperature dependence, and the morphology of the martensitic transformation in a Cu-Zn-Al alloy was studied. The hysteresis behavior of the cyclic transformation, as characterized by following the change in electrical resistivity accompanying the transformation changed in two respects: First, the M_s and A_f temperature shifted to higher temperatures while the M_f and A_s temperatures remained constant. Secondly, the amount of martensite undergoing cyclic transformation decreased. These changes appeared to saturate at 300 cycles and could be partly recovered during room temperature aging. the morphology and mode of transformation also changed. During the first few cycles, transformation occurred in two simultaneous ways: 1) as martensite plates which are observed to grow and thicken in a continuous manner and 2) as plates which form in a "burst" process. After 60 cycles no "burst" type transformation occurred during cooling and plate growth and thickening was stepwise.

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THE EFFECT OF THERMAL CYCLING ON THE THERMOELASTIC MARTENSITIC
TRANSFORMATION IN A Cu-Zn-Al ALLOY

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ABSTRACT

The effect of thermal cycling between the M_f - A_f on the thermal hysteresis, temperature dependence, and the morphology of the martensitic transformation in a Cu-Zn-Al alloy was studied. The hysteresis behavior of the cyclic transformation, as characterized by following the change in electrical resistivity accompanying the transformation changed in two respects: First, the M_s and A_f temperature shifted to higher temperatures while the M_f and A_s temperatures remained constant. Secondly, the amount of martensite undergoing cyclic transformation decreased. These changes appeared to saturate at 300 cycles and could be partly recovered during room temperature aging. the morphology and mode of transformation also changed. During the first few cycles, transformation occurred in two simultaneous ways: 1) as martensite plates which are observed to grow and thicken in a continuous manner and 2) as plates which form in a "burst" process. After 60 cycles no "burst" type transformation occurred during cooling and plate growth and thickening was stepwise.

I. Introduction

The effects of transformation cycling on the nature of the thermoelastic martensitic transformation in ferrous alloys has been extensively studied.(1,2) Changes in the M_s temperature and the extent of thermal hysteresis are attributed to the order-disorder reaction in ferrous alloys.(2) This is in contrast to the case of the thermoelastic martensitic transformation in the beta brass system where the alloy is initially completely ordered after quenching, and remains ordered through the transformation. While there have been several studies which bear on the effects of thermal cycling on the subsequent martensitic transformation in beta brass systems, the data are sparse and the results contradictory. Earlier work(3) reported that in a Cu-40.6 wt% Zn alloy the M_s temperature increased about 5°C after 50 thermal cycles. However, later work(4) on a Cu-39.63 wt% Zn alloy reported that the M_s temperature decreased about 3°C after 20 thermal cycles. Moreover, it is clear that no detailed and systematic studies on the effect of thermal cycling on the martensitic transformation in beta brass systems have yet been reported.

The purpose of this study is to examine in detail the effect of thermal cycling between the M_f and A_f temperatures on the thermoelastic martensitic transformation in a Cu-Zn-Al alloy. The transformation was described by its characteristic temperatures, M_s , M_f , A_s , A_f , and thermal hysteresis behavior as determined by electrical resistance vs. temperature measurements and the morphology of the transformation by examining optically the surface relief during thermal cycling.

II. Experimental Method

Specimen preparation: The alloy studied had a nominal composition of 29 wt% Zn, 3 wt% Al and the balance Cu. The alloy composition was defined on the

one hand to maintain an electron concentration of 1.4 to stabilize the beta phase and on the other hand to obtain transformation near room temperature for experimental convenience. The alloy was prepared by melting Cu (99.99%) powder, Zn (99.9 wt%) ingot and Al (99.999%) wire in a sealed quartz tube under an argon atmosphere. After melting and solidification, the ingot was annealed in the quartz tube at 850°C for one week. After annealing the ingot was cold rolled into a 1-mm thick strip. To form the beta phase these strips were heated in air at 850°C for 5 seconds (to limit Zn loss during heating) and then quenched into an iced 10% NaOH solution. The strips were then electropolished in orthophosphoric acid at room temperature to remove approximately 0.1 mm from each surface, removing oxides and possible surface dezincification. After electropolishing, some martensite was observed on the specimen surface which may have originated from quenching stresses or electropolishing. These were observed not to enter the thermoelastic transformation as had been suggested previously.⁽⁵⁾ These martensitic regions were minimized by alternating the electropolishing conditions.

Electrical resistance-temperature hysteresis measurement: The transformation behavior of the alloy was followed by measuring the electrical resistance as a function of temperature through the transformation thermal cycle. The resistivity specimen was 8 cm long and 1 x 3 mm in cross section. Four copper leads were spot-welded, two to each end of the specimen for current supply and potential measurement. In addition, a chromel-alumel thermocouple was spot-welded to the center of the specimen in order to monitor temperature. The specimen was immersed into a stirred alcohol bath maintaining a temperature uniform to $\pm 0.1^\circ\text{C}$. A thermal change rate of $3^\circ\text{C}/\text{min}$ was used for the cyclic transformation hysteresis measurements.

Temperature and electrical resistance were then measured continuously using a fast response X-Y recorder. It was observed that the transformation hysteresis data obtained were rate-independent at this and lower heating and cooling rates. For all tests, hysteresis curves obtained for adjacent transformation cycles were perfectly coincident within the sensitivity of the measurements.

Optical metallography: The morphological changes occurring during the cyclic transformation process were followed using a heating-cooling stage on an optical metallograph. For these observations the rates of cooling and heating were controlled to $1^{\circ}\text{C}/\text{min}$.

Thermal cycling between those for which resistance measurement metallographic observations were made, was accomplished by alternating the specimen between baths of hot water ($\sim 38^{\circ}\text{C}$) and cold alcohol (-20°C). At each temperature the specimen was held for 10 seconds in order to complete the transformation and minimize any aging effects.

In order to correlate the optical observations with the electrical resistance hysteresis data the same specimen was used for both observations. Because the specimen was initially quenched into ice water to assure the formation of the ordered beta phase, the first transformation cycles studied were actually the second cycle for the optical observations, and the third cycle for the electrical resistance measurement.

III. Results and Discussion

Hysteresis data: After the initial electrical resistance-temperature hysteresis loop was determined for the complete transformation, the specimen was cyclically transformed for a number of thermal cycles between 38°C and -20°C , and the hysteresis behavior again measured. The data obtained are

shown in Figure 1. By comparing curves a to d it is apparent that the transformation characteristics have changed during cycling as follows: first, the M_s and A_f temperatures increased while the M_f and A_s remained constant; second, the area of the hysteresis loop decreased with cycling; third, the electrical resistance of the specimen after reversion increased with cycling while the electrical resistance of the specimen transformed to martensite remained constant. There are two possibilities which may account for the latter observation. First, the β -phase could be plastically deformed during thermal cycling. Second, the reversion process could be incomplete and some martensite become retained above the measured nominal A_f temperature. Since the electrical resistance and the slope of the resistivity vs. temperature curve below the M_f temperature are cycle-independent, it is unlikely that the first explanation is correct. Moreover, if the β -phase was plastically deformed, one would expect that the slope of the resistivity vs. temperature curve above the A_f temperature would decrease with increased cycling. It is therefore likely that, with cycling, some martensite becomes retained above the reversion temperature, the nominal A_f , reducing the total extent of the thermoelastic transformation. The unrelaxed elastic strain accompanying the transformation could act to stabilize the martensite in these bulk specimens. The relative amount of this retained or unreverted martensite can be estimated from Figure 1. Extrapolating the straight line from A_s to higher temperature, the height between this line and the M_s should be proportional to the amount of martensite undergoing reversible transformation. As shown in Figure 2, the effects of cyclic transformation on the M_s and A_f temperatures as well as the extent of the reversible transformation decreased with increasing cycling, and appeared to saturate at approximately 300 cycles. One might also speculate

as to the effect of the thermal cycle and specimen size on generating thermally induced residual stresses which could alter the hysteresis behavior. However, the development of thermally induced stresses is considered unlikely since the temperature change per cycle, 58°C , is small as compared with the 820°C quench needed to initially retain the beta phase in these relatively thin, 1 mm thick, specimens.

Aging response: In order to test the response of this alloy system to potential aging effects during the transformation cycle, one specimen was cycled and its electrical resistance-temperature hysteresis response measured as described in the previous section through 60 transformation cycles, held for 16 days at room temperature and then its hysteresis behavior remeasured. The data obtained are shown in Figure 3. Comparing the curves shown, a -after the third cycle, b -after the 60th cycle, and b' -after the room temperature hold, it is evident that the hysteresis response of the specimen recovered to some degree during the room temperature hold. Aging behavior has been observed previously(6) for a Cu-Zn-Al alloy where the degree of order and the M_s temperature was altered by heat treatment and subsequently recovered after aging at room temperature. For that observation the recovery process was associated with reordering of the thermally disordered alloy. In the present study, it is unlikely that either the cycling effects or the subsequent aging behavior can be associated with changes in the degree of order since as shown in Figure 1 and Figure 3, the resistance of transformed martensite at the M_f and hence the extent of transformation below the M_f is unaffected by either cycling or aging.

Transformation Morphology

Martensite transformation during second cycle: Figures 4(a) - (d) show a

series of micrographs taken during cooling through the second transformation cycle. The cooling rate was slow enough so that "equilibrium" conditions could be reached. Figure 4(a) and (b) showed that during cooling two types of martensite transformation processes were observed. In the first, martensite plates grew continuously. Such growth is shown in the area marked by arrows in Figure 4(a) and (b). The velocity for plate extension was higher than for thickening. For the plates shown, the elongation rate was about $300 \mu/^{\circ}\text{C}$ while thickening at a rate about $130 \mu/^{\circ}\text{C}$. In the second type of transformation, plates grew in a "burst" mode in the regions between the continuously growing plates. This "burst" type of growth occurred at the position marked b in the micrographs, although these two modes of transformation occurred simultaneously in different regions of the specimen. In general, in any one area the continuously formed plates transformed first and then transformation occurred by a "burst" process in the region of the β -phase bounded by previously formed plates. It is suggested that the "burst" mode is the result of a relaxation process, releasing the elastic strain accompanying the formation of the previous martensite, by the formation of different self-accommodating variants. It was also observed that the martensite transformation occurred at different temperatures in different grains of the same specimen. In following the transformation during cooling in grains α and β in Figure 4, it is obvious that no transformation had occurred in the β -grain at 14°C while most of the α -grain had already transformed to martensite. At 11°C , transformation just began to start in the β -grain. In the α -grain transformation was completed within a 6°C interval, although the transformation for all the grains in the entire polycrystalline specimen occurred over a 40°C interval as observed in the electrical resistance-temperature hysteresis measurement. Figures 4(e) and

(f) shows the features of the reversion process during the heating portion of the second thermal cycle. The region pointed to by the arrow at C in Figure 4(f) shows the shrinkage process for the continuously formed plates. For this structure, as seen by comparing Figure 4(f) and Figure 4(a), the thermal hysteresis between martensite formation and reversion was less than 4°C . Figure 4(e) shows the reversion of the plates formed by the burst process. In the region marked b on these figures, by comparing Figure 4(e) and Figure 4(d), the martensite plates which formed by a burst mode were also observed to disappear by a burst mode. For these burst plates, the thermal hysteresis was about 7°C . For the fine burst plates shown at b' in Figure 4(d) and Figure 4(f) the thermal hysteresis approached 8 to 10°C . In general, 10°C was the largest thermal hysteresis observed for a single martensite plate.

Martensite transformation after 60 cycles: The structure obtained during the 61st thermal cycle is shown in Figures 5(a) through (d). These optical micrographs were taken from the same area and under the same conditions as shown previously for the second cycle. The grain boundaries were used to identify the equivalent positions in the two series of micrographs. Figures 5(a), (b), and (c) show the transformation to martensite during cooling. By comparing Figure 4 with Figure 5, it is evident that the martensite plates formed in the same position during the 61st cycle as in the second cycle. The martensitic plates pointed to by the arrows at the top of these micrographs show that during cooling, fine parallel lines joined together step-by-step forming a large V-shaped martensite plate. By contrast, as shown in Figure 4(a) and (b) at this identical position, during the second thermal cycle martensite plates formed by a continuous growth mode. The arrows shown in the middle of each of these series of micrographs, i.e., (a) through (c), follow

the formation of different martensite variants which each grew in the same stepwise manner. This is in contrast to the observation of the second thermal cycle, where in this identical position the martensite variants formed by a burst mode. Figure 5(d), taken during the heating portion of this thermal cycle, shows that reversion occurred in the reverse step-by-step formation as observed during martensite formation. But during the second cycle this same grain reversion occurred by two modes, continuous shrinkage and "burst."

IV. Conclusions

The effect of thermal cycling between the M_f - A_f on the thermal hysteresis, temperature dependence, and the morphology of the martensitic transformation in Cu-Zn-Al showed that the hysteresis behavior of the cyclic transformation changed in two respects. First, the M_s and A_f temperature shifted to higher temperatures while the M_f and A_s temperatures remained constant. Secondly, the amount of martensite undergoing cyclic transformation decreased. These changes appeared to saturate at 300 cycles and could be partly recovered during room temperature. The morphology and mode of transformation also changed. During the first few cycles, transformation occurred in two simultaneous ways: 1) as martensite plates which are observed to grow and thicken in a continuous manner and 2) as plates which form in a "burst" process. After 60 cycles no "burst" type transformation occurred during cooling and plate growth and thickening was stepwise.

V. Acknowledgement

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FIGURE CAPTIONS

- Figure 1. Electrical resistance vs. temperature hysteresis behavior of the Cu-29 wt% Zn - 3 wt% Al alloy for the 3rd, 60th, 180th, 300th and 400th thermal cycle.
- Figure 2. Variation of the M_s , A_f temperatures and the relative amount of martensite undergoing thermoelastic transformation as a function of transformation cycle.
- Figure 3. Aging effect, plots of electrical resistance vs. temperature hysteresis behavior. Curves a and b, the 3rd and 60th thermal cycle respectively. Curve b' was measured on a specimen which had first undergone 60 thermal cycles, held at room temperature for 15 days, and then recycled.
- Figure 4. A series of optical micrographs showing the progress of martensitic transformation during the second thermal cycle. Cooling and heating rates $1^\circ\text{C}/\text{min}$.
- Figure 5. A series of surface relief micrographs obtained during the 61st thermal cycle of the same area as shown in Figure 4.

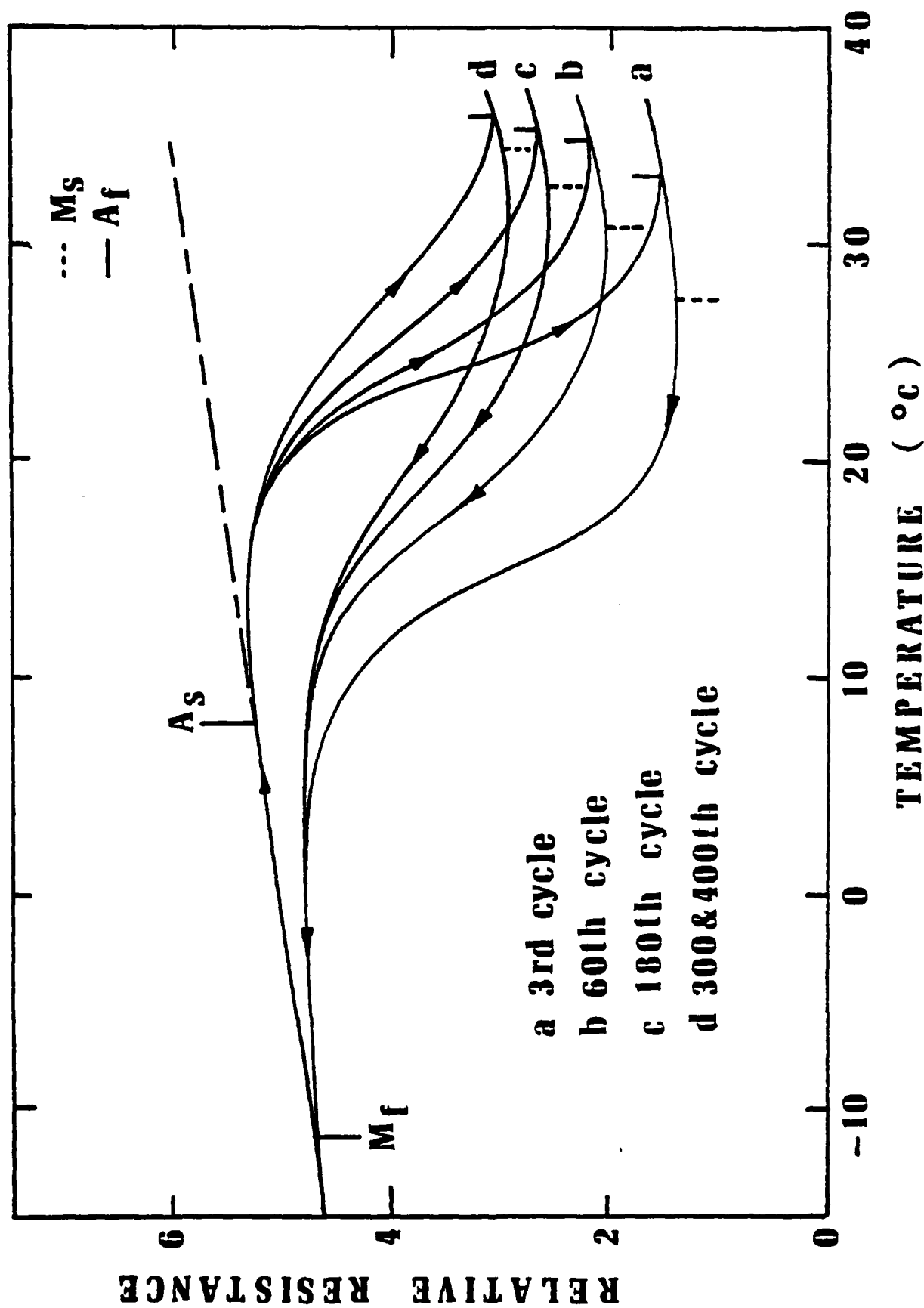


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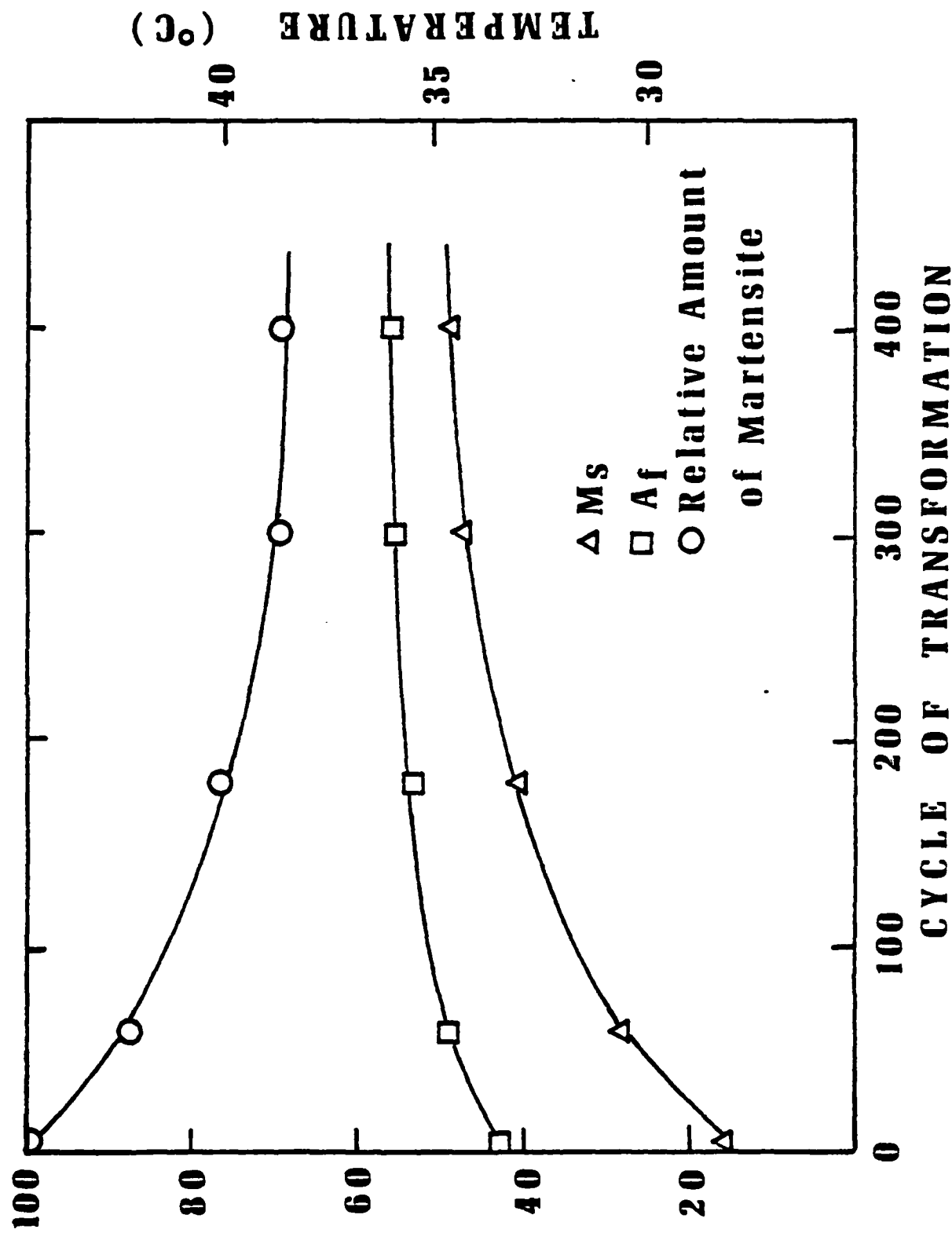


Figure 2. Variation of the M_s , A_f temperatures and the relative amount of martensite undergoing thermoelastic transformation as a function of transformation cycle.

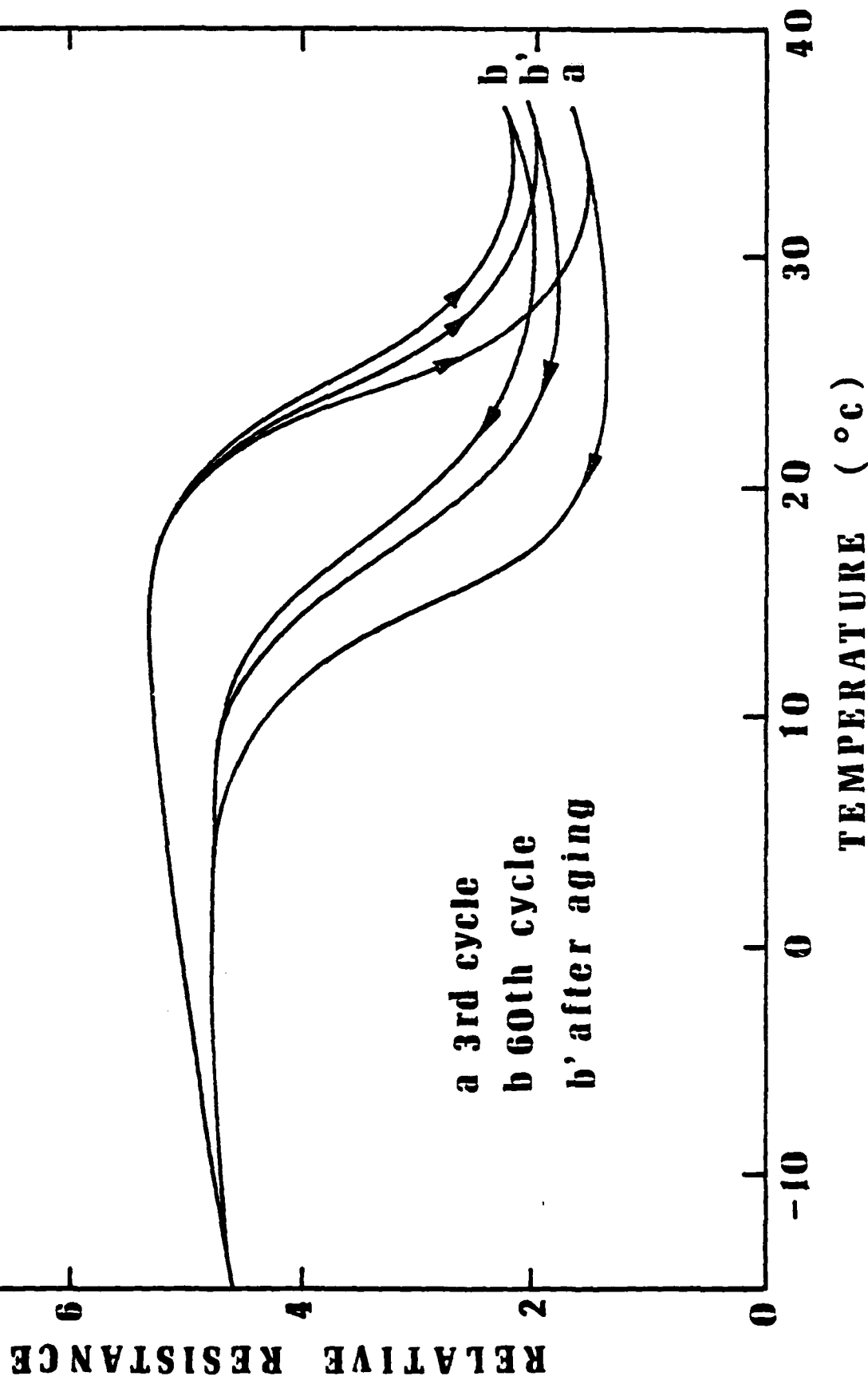
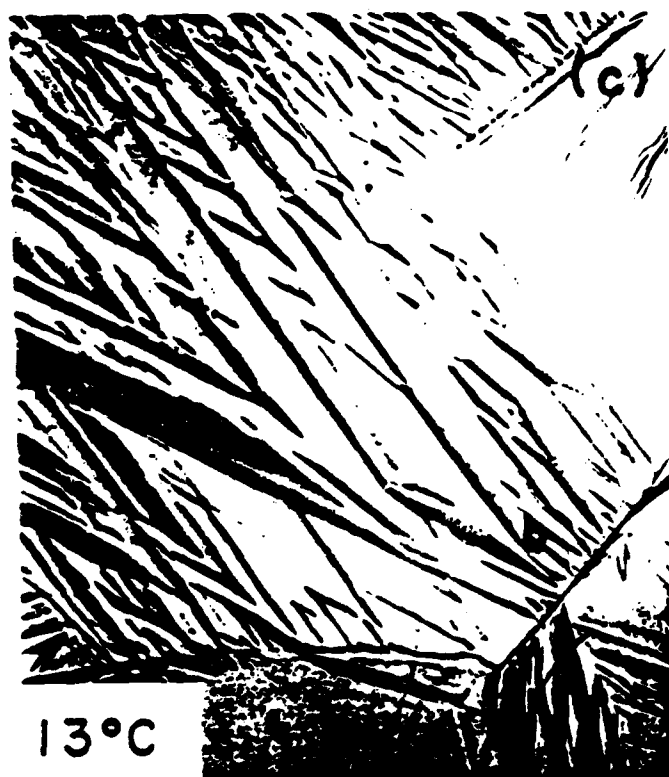


Figure 3. Aging effect, plots of electrical resistance vs. temperature hysteresis behavior. Curves a and b, the 3rd and 60th thermal cycle respectively. Curve b' was measured on a specimen which had first undergone 60 thermal cycles, held at room temperature for 16 days, and then recycled.



Cooling →



Cooling →

Figure 4.

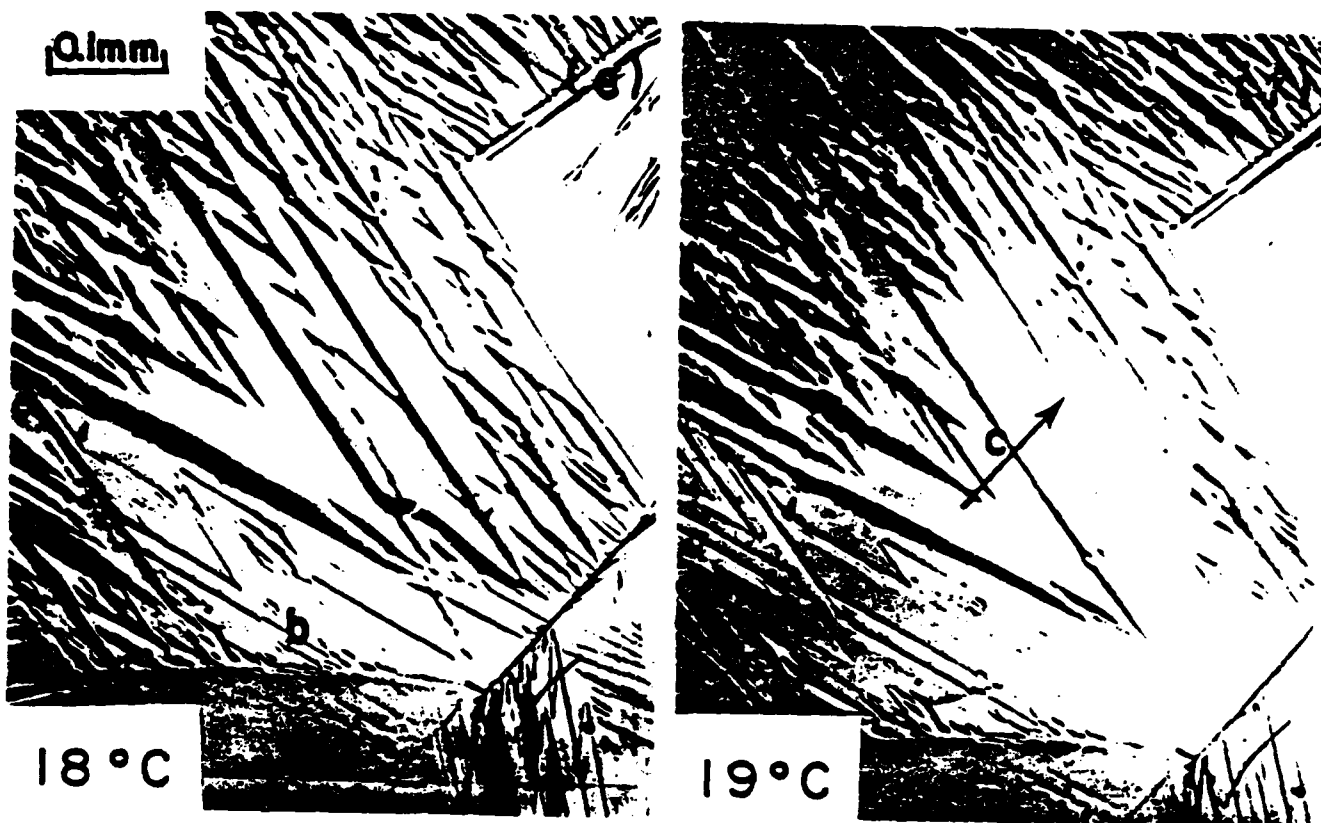


Figure 4



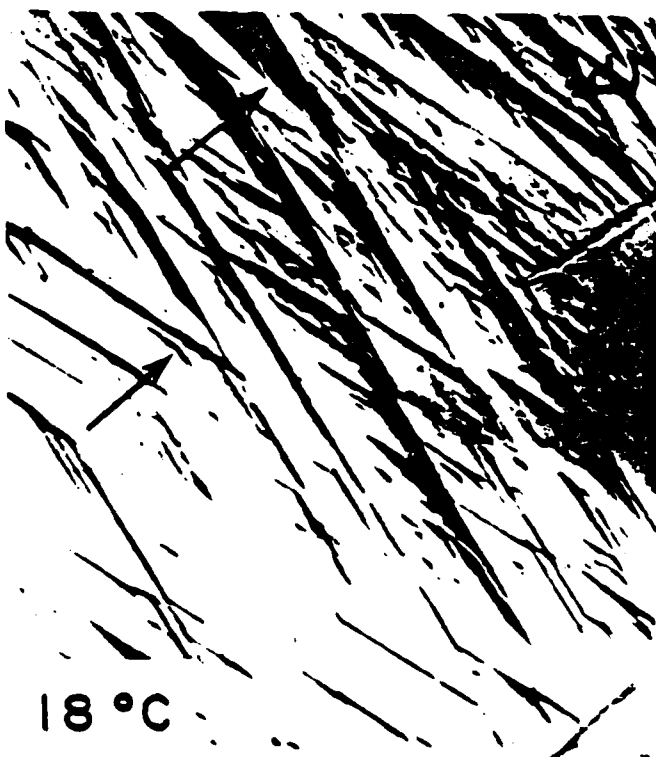
Cooling



Cooling



Cooling



Heating

Figure 5.

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