

Martensitic Transformation Cycling Effects in Cu-Zn-Al Shape Memory Alloys

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The effects of transformation cycling between the parent (P) and martensite (M) phases of selected Cu-Zn-Al alloys were studied. Using differential scanning calorimetry it was observed that the martensite start temperature, M_s , progressively shifts upward with cycling. Also, the proportion of the microstructure actually undergoing $P \leftrightarrow M$ transformation decreases. Transmission electron microscope observations reveal dislocation substructures generated by martensite transformation and reversion.

I. INTRODUCTION

CERTAIN alloys have the unusual ability to recover an original shape after undergoing what would appear to be, because of the magnitude of the strain involved, permanent deformation. These so-called "shape memory effects" are a direct result of thermoelastic martensitic transformation. In such transformations a balance is struck between the chemical free energy change which accompanies the transformation and the elastic energy built up around the martensite crystallites. The $P \rightarrow M$ transformation can be induced by either a decrease in temperature or an increase in stress, with martensite plates forming and growing continuously as temperature decreases and/or as stress increases, and with these plates shrinking away to reform the original parent phase as temperature is increased and/or as stress is decreased. The $M \rightarrow P$ reversion is accomplished microstructurally by the exact reverse path of the $P \rightarrow M$ transformation. In most shape memory alloys there are several temperature or stress-related crystallographic routes to induce martensite crystallites from the parent phase, whereas for each martensite crystallite there is only one crystallographic route back to the parent phase, namely, the path along which that particular crystallite has been created. Another way to explain this is to point out that martensite crystallites must nucleate within original parent phase grains, but that the converse is not true; the parent phase reforms without nucleation within or from the martensite microstructure, but rather by shrinkage reversion of the numerous martensite crystallites to reform a given grain. Therefore, if the alloy is deformed such as to induce or revise a martensitic microstructure, it may regain its original, prestress shape when temperature and/or stress is changed such as to make the parent phase stable once again.

It is implicit in the concept of thermoelastic martensitic transformation that there is no irreversible behavior involved in the $P \leftrightarrow M$ transformations, *i. e.*, no plastic deformation. However, there is some indirect evidence that thermoelastic behavior is limited by the yield strength of the parent phase¹ and that at least in the first $P \leftrightarrow M$ cycles the transformation may not be perfectly thermoelastic.² Furthermore, there is direct evidence of the production of dislocation substructural debris as a result of transformation

cycling.³ In order to clarify and explain these observations, the present work was initiated to study the effects of multiple thermal cycles on the $P \leftrightarrow M$ transformation kinetics of selected Cu-Zn-Al shape memory alloys and to correlate this with the substructural condition of the microstructure as transformation cycling proceeds.

II. EXPERIMENTAL

The alloy studied in this work was provided by Delta Metals Research Ltd., Ipswich, Suffolk, England, with a nominal composition of 69.25 wt pct Cu-26.75 wt pct Zn-4.0 wt pct Al and a reputed M_s temperature of about 270 K. This material, originally in the form of 1 cm diameter hot-worked bar, was machined into discs 3 mm in diameter and 0.4 mm thick which were sealed in evacuated quartz tubes, solution treated 15 minutes at 900 °C, and quenched in water. Transformation cycling, usually of a single disc, was carried out in a Perkin-Elmer Model DSC-2 differential scanning calorimeter at a rate of 10 K per minute between 240 K and 340 K, which spans the M_f to A_f temperature range for this alloy. The characteristic transformation temperatures, M_s , M_f , P_s , P_f , as well as other kinetic parameters, are defined schematically in Figure 1.

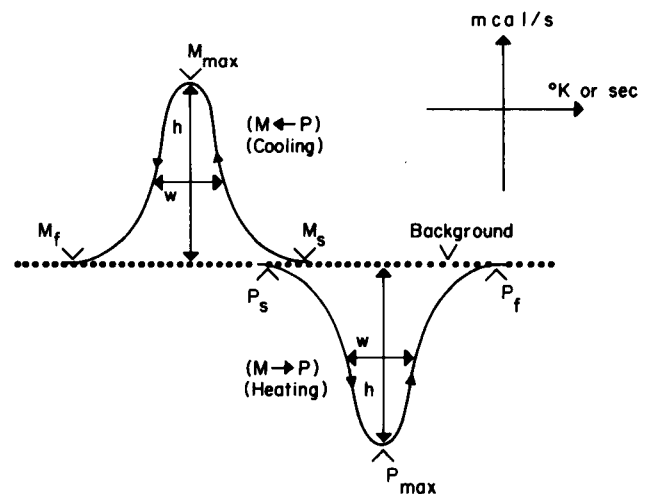


Fig. 1 — Schematic differential scanning calorimeter profiles for the $P \rightarrow M$ and $M \rightarrow P$ transformations, defining the kinetic parameters, including the transformation temperatures M_s , M_{max} , M_f , P_s , P_{max} , P_f and the peak height and peak width at $1/2$ -height.

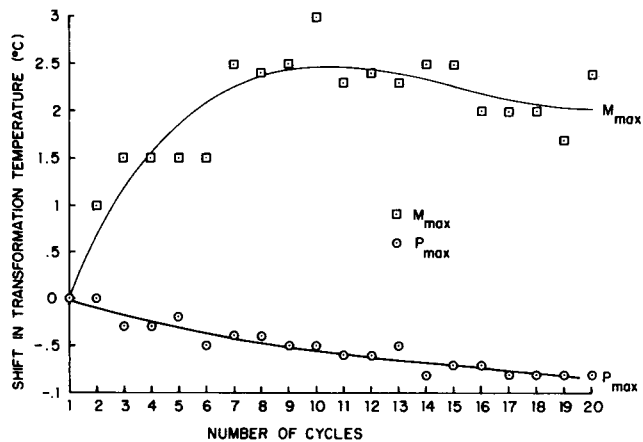
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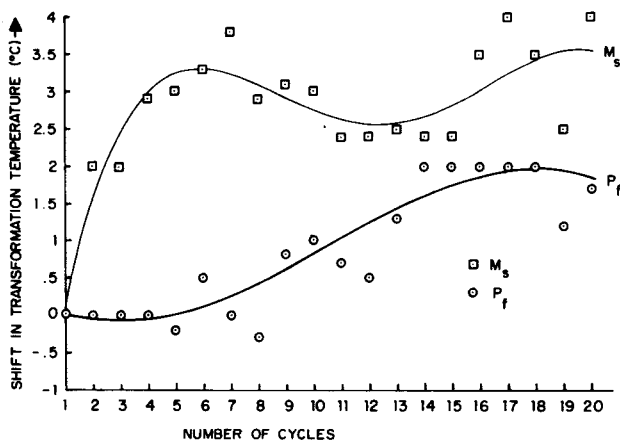
Polynomial curve fitting techniques were used in the reduction of all data. Thin foils for transformation electron microscopy were prepared from bulk samples subsequent to cycling in the DSC. The microstructures before and after transformation cycling were compared.

III. RESULTS AND DISCUSSION

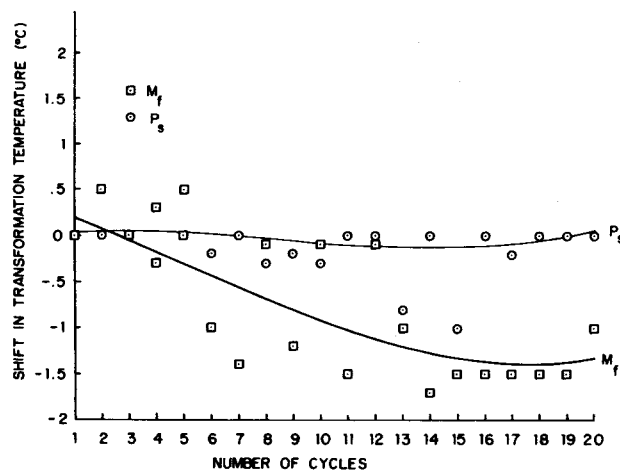
As a result of transformation cycling, calorimetric data show that M_s , P_f , and M_{max} all rise, while M_f and P_{max}



(a)



(b)

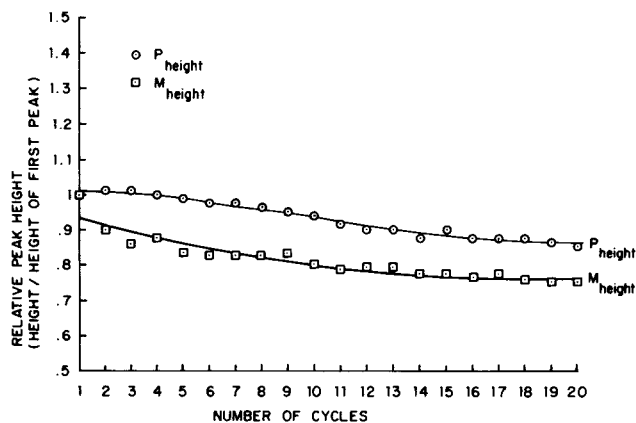


(c)

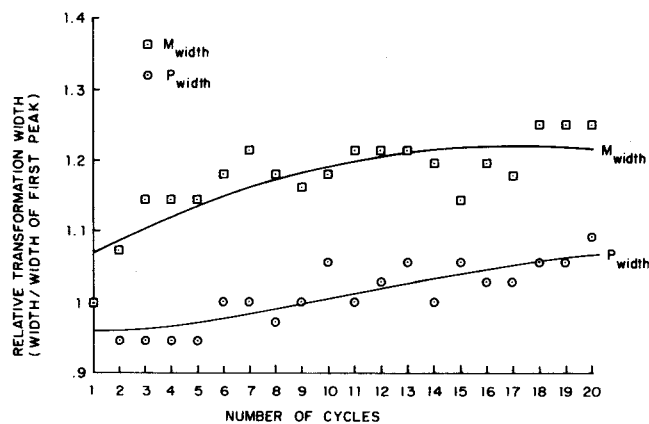
Fig. 2—Variation of the transformation temperatures with cycling between 240 K and 340 K (a) M_{max} and P_{max} vs number of complete transformation cycles, (b) M_s and P_f , and (c) M_f and P_s .

decrease and P_s is virtually unaffected; these data are presented in Figure 2. At the same time, both the M and P transformation peaks are becoming somewhat more spread out, *i. e.*, becoming lower and wider, as shown in Figures 3(a) and 3(b). Also, as a result of the relative shifts of the M and P peaks, the transformation hysteresis decreases slightly, from about 13 deg to 10.5 deg, as shown in Figure 3(c). All these effects are summarized schematically in Figure 4.

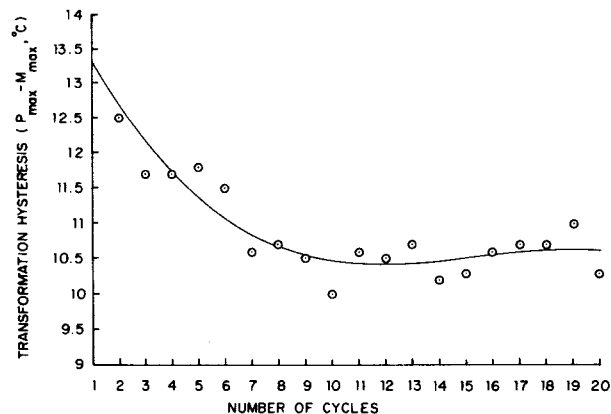
In considering the appropriate interpretation of this kinetic data, a model was invoked which conceives of the



(a)



(b)



(c)

Fig. 3—Variation of the DSC peak shape and transformation hysteresis due to cycling between 240 K and 340 K (a) peak heights vs number of cycles, (b) peak widths vs number of cycles, and (c) transformation hysteresis, $P_{max} - M_{max}$, vs number of cycles.

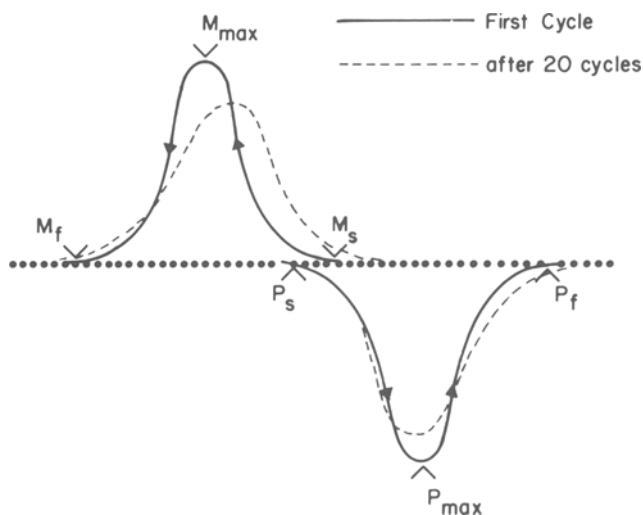


Fig. 4—Schematic summary of the changes in the DSC transformation profiles with cycling.

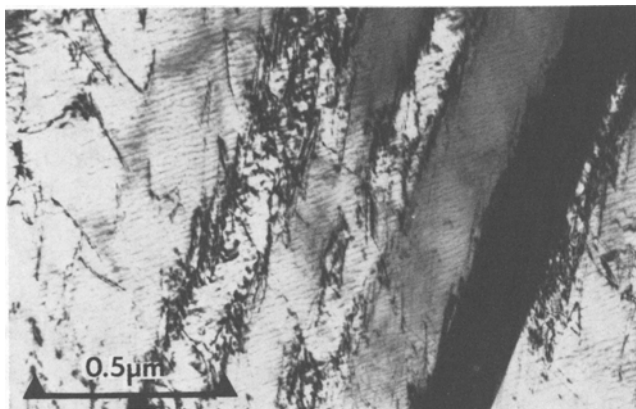


Fig. 5—Dislocation arrays left behind in the parent phase by reverted martensite plates.

establishment, through repeated transformation, of a fixed hierarchy of nucleation sites which enhances the establishment of a reproducible and reversible martensitic microstructure.⁴ It has been shown many times⁵⁻⁹ that one of the characteristics of thermoelastic martensite is that each plate in the microstructure appears in the same place each time the alloy is cooled from M_s to M_f . The plates appear in the same sequence each time on cooling and revert in the exact opposite order on reheating, *i. e.*, the first plate to form is the last to revert, and so on. This suggests that a fixed distribution of predisposed nucleation sites, as well as a certain hierarchy of instability at these sites, has been established in the microstructure. However, it has never proved possible to record an image (for example, in transmission electron microscopy) which unequivocally establishes the association of an embryonic martensite plate with a nucleating defect; this may be due largely to the statistical problem of locating such an event at high magnification. The kinetic data collected in this study are consistent with the establishment, or enhancement, of a hierarchy of incipient nucleation sites as cycling progresses, although in itself the kinetic data do not describe or locate these sites. One might argue that as the preferred sites are stimulated by repeated activation,

they become more prominent, so that martensite nucleates more readily; for example, M_s increases (Figure 2(b)).

Some years ago, Pops and Massalski¹⁰ established that martensitic transformations in β -phase alloys such as Cu-Zn have two stages on cooling, a “thermoelastic” or slow-growth stage and a “burst” stage, with the occurrence of the burst martensite diminishing and vanishing altogether during multiple thermal cycling. Pops and Massalski have also shown that the formation of burst martensite produces lattice defects and some degree of plastic deformation in the parent lattice.¹⁰ Recently, Kajiwara and Kikuchi¹¹ have published TEM evidence that thermal cycling introduces dislocations into the parent phase of Cu-Zn alloys. In the present work, TEM observations also indicate the generation of dislocation substructure in multiple-cycled samples, and that this substructure serves to stabilize the martensite. For example, in Figure 5, in a sample that is, when at room temperature, about 20 K above the P_f temperature as recorded in the calorimeter, one observes isolated residual plates of martensite and a clear association of them with dislocation structures which the martensitic transformation itself has created. In uncycled samples of this alloy, the microstructure consists of a homogeneous β_1 parent phase with low dislocation density; occasionally an isolated martensite plate is seen in an uncycled sample, but they are much fewer and without the attendant dislocation substructure seen in cycled samples. These dislocations constitute irreversible features introduced by the transformation cycling process. It may be expected that this dislocation substructure serves to strengthen locally the parent phase, that is, increases its resistance to further plastic deformation. This in turn will improve the reversibility of the martensitic transformation, *i. e.*, the thermoelastic nature will be enhanced.

At the same time as the M peak is shifting upward in temperature, the P peak does not seem so much affected (see Figure 4). M_s and M_{max} shift much more than P_f and P_{max} . This can be explained by considering that whereas the $P \rightarrow M$ transformation depends on nucleation of new martensite crystallites from the parent phase, the reverse, $M \rightarrow P$, transformation does not. The $M \rightarrow P$ reversion process simply involves shrinkage of the existing martensite crystallites back to the parent phase.

Accompanying the relative shifts in M_{max} and P_{max} is a decrease in the transformation hysteresis, defined here as $P_{max} - M_{max}$, a measure of the overlap of the $P \rightarrow M$ and $M \rightarrow P$ transformations. Due to cycling, a proportion of the martensite is obviously stabilized at temperatures above the apparent P_f , and martensite can renucleate more readily (*i. e.*, at higher temperature) on cooling toward M_s . This stabilization of the martensite phase is evidenced by the increase in M_s as well as the somewhat lesser increase in P_f . Martensite nucleates at higher temperatures on cooling (higher M_s), due apparently to some sort of nucleation site enhancement, and around these same nucleation sites reversion is inhibited to higher temperatures (higher P_f) on reheating. The increasing width of the M and P peaks is related mainly to these M_s and P_f shifts. All these factors indicate that the martensite is able to exist over a wider range of temperature, and therefore we may say that thermal cycling has a stabilizing effect on the martensite relative to the parent phase.

Perhaps one of the most interesting results is that as the number of thermal cycles increases, the apparent amount of

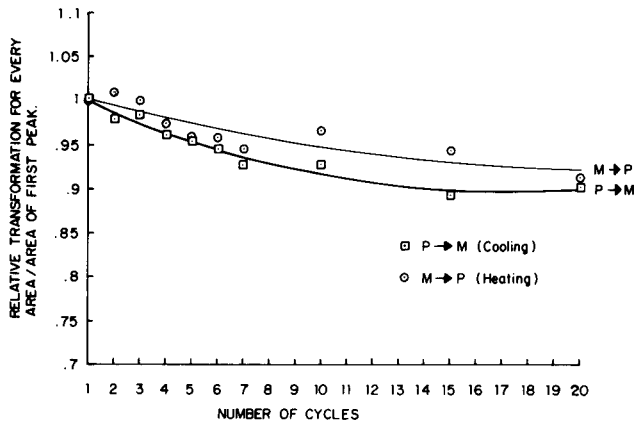


Fig. 6—Variation in total transformation energy with cycling.

transformation taking place during both the cooling and heating cycles, as measured by the total heat of transformation in the calorimeter, decreases (Figure 6). Clearly, less and less material undergoes transformation with each cycle, although the effect seems to saturate, as do all the temperature shifts, after about a dozen cycles. Either some martensite is retained on heating above the apparent P_f or some parent phase is retained on cooling below the apparent M_f . The microstructural evidence supports the former proposition. Furthermore, we may notice that it is the phase whose formation depends on nucleation phenomena, namely, the martensite, which is stabilized, and we may reasonably conclude that this is due to the enhancement of the nucleation mechanism for individual crystallites. Certain martensite crystallites in the hierarchy are, in fact, so stabilized that they never revert over the temperature range studied, which extends to about 40 K above the apparent P_f .

Clearly, the $P \leftrightarrow M$ transformation, especially over the first few cycles, is not a completely reversible process, *i. e.*, is not perfectly thermoelastic. Some degree of irreversible behavior takes place during these initial cycles, as evidenced by the generation of substructural dislocations (Figure 5) and the reduction in the total energy of transformation (Figure 6). After a certain number of cycles (about 10 to 12) a saturation of this effect is reached, and the parameters remain nearly constant with further cycling. Further cycles become completely reversible in nature, that is, with a given cycle having all the same kinetic parameters as the preceding cycle. As further support for this, it can be noted that during initial cycling, the DSC peaks often (it depends on the resolution setting of the instrument) show secondary structure on the primary peaks (what might be called a noisy background), but as cycling proceeds, the peaks smooth out. This suggests on the microstructural scale a smoothing out of the transformation process, perhaps involving the cessation of the burst phenomenon reported by Pops and Massalski.¹⁰ An analogy could be made to the process of creating a trail through initially unbroken forest or brush-

land. The first time the path is taken, travel is difficult and sporadic. But as the path is traveled back and forth several times, the trail becomes more and more established until eventually steady progress can be made and no further significant improvements in the trail are possible. In the present terms, the trail-making seems to be connected to the generation of dislocation substructure initially not present.

IV. SUMMARY

The kinetic and microstructural observations made in this work indicate that thermal transformation cycling generates substructural dislocations, establishes favored nucleation sites for martensitic transformation, locally strengthens the parent phase, and stabilizes the martensite phase over a wider temperature range. As a result of transformation cycling, M_s and A_f rise, transformation hysteresis decreases, and the proportion of the microstructure transforming decreases. Transmission electron microscopy reveals the generation of dislocation substructure and associated stabilization of martensite. This substructure is associated with enhanced martensite nucleation and resistance to reversion of certain martensite crystallites in connection with a hierarchy of incipient nucleation sites inherent in the parent phase. With perhaps 10 to 12 complete thermal cycles, the cycling effects saturate and thereafter the proportion of the microstructure transforming does so in a completely reversible fashion, *i. e.*, the $P \rightarrow M$ transformation becomes truly thermoelastic.

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