

Martensite destabilization in $\text{Au}_7\text{Cu}_5\text{Al}_4$ shape-memory alloy

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Aging-induced changes in the austenite peak (A_p) temperature of the $\text{Au}_7\text{Cu}_5\text{Al}_4$ shape memory alloy are investigated. Whereas heat-treating the parent phase at temperatures above 140°C, or aging the martensite for long times at room temperature, both stabilized the A_p to about 80°C, low temperature excursions into the parent phase cause the subsequent A_p to drop to about 60°C and the transformation hysteresis to decrease. The evidence indicates that this de-stabilization of the martensite is caused by time-dependent relaxation of elastic constraint due to parent-phase lath migration during the preceding low-temperature austenitizing treatment. This mechanism of aging is different to that of the better-known SC-SRO phenomenon.

1. Introduction

Time-dependent effects in shape memory alloys (SMAs) can change the temperatures at which their characteristic displacive phase transformations occur. This is undesirable as reproducible values of the martensite start (M_S) and austenite start (A_S) temperatures (*ie.* ‘cyclic stability’) are needed for most technological applications of SMAs^{1,2}. The situation for Cu-, AuCd- and TiNi-based SMAs has previously been investigated in some detail, and at least five principle mechanisms of aging or “relaxation” have been identified: these are (1) the symmetry-conforming short-range order phenomenon (SC-SRO) which removes martensite anti-site defects^{2,3}, (2) elimination of quenched-in vacancies^{4,5}, (3) non-conservative relaxation of elastic stresses⁶, (4) transformation-induced generation of dislocations⁶⁻⁸ and (5) decomposition of the β -phase and/or precipitation of second phases^{3,9-12}.

A β -electron compound with the stoichiometry $Au_7Cu_5Al_4$ (sometimes known as ‘Spangold’^{13,14}) has shape-memory properties, and is of interest because it is radio-opaque, relatively corrosion-resistant and 18 carat. $Au_7Cu_5Al_4$ is one of the possible stoichiometries in the ternary β -phase system $Au_xCu_{12-x}Al_4$ ($0 < x < \sim 7.5$)¹⁵⁻¹⁷, and its highest temperature structure has been taken in the past to be A2¹⁸⁻²⁰, *ie.* ordinary body-centred cubic. Recently, however, it has been shown (Cortie *et al.*, submitted) using *in situ* synchrotron diffraction experiments that $Au_7Cu_5Al_4$ melts directly from the B2 phase and that it does not pass through the A2 structure. There is, however, a phase transition at about 630°C which has now been confirmed as being due to the $L2_1 \leftrightarrow B2$ transformation and not $B2 \leftrightarrow A2$ as previously supposed. In any event, the parent phase of the martensite in $Au_7Cu_5Al_4$ is usually $L2_1$ structured²¹.

The thermo-elastic phase transformations in $\text{Au}_7\text{Cu}_5\text{Al}_4$ freshly quenched from temperatures $>630^\circ\text{C}$ (a state that we will designate here as ‘beta-quenched’) are often weak or even absent, however, a few minutes of aging of the parent phase in the temperature range 100 to 300°C changes the nature of the transformation and strongly increases the intensity of the phenomena associated with both the formation of martensite and its reversion back to austenite^{17, 22, 23}. It is reasonable to accept that a high concentration of vacancies, anti-site defects, dislocations and/or lack of properly developed ordering in freshly beta-quenched material inhibits the phase transformation. This is reportedly the case in many other coinage metal SMAs^{24-30, 31}. Development of the equilibrium structure when beta-quenched samples of $\text{Au}_7\text{Cu}_5\text{Al}_4$ are reheated is believed to be indicated in thermal analysis experiments by a weak endothermic peak observed at 130 to 140°C ^{22, 23}.

However, it has been noted that thermal history and aging continue to have some effect on the transformations of $\text{Au}_7\text{Cu}_5\text{Al}_4$ even after the first thermo-elastic cycle. In particular, the A_S and M_S temperatures can vary by up to several degrees Celsius depending on heat treatment^{17, 22, 23}. Urbano *et al.* have investigated the effect of aging on transformation of the martensite and parent phases of $\text{Au}_7\text{Cu}_5\text{Al}_4$ and derived an activation energy of 1.1 eV for aging processes in the martensitic condition. Aging in the martensite was ascribed by them to the SC-SRO phenomenon and could raise the A_P by up to 4°C . In contrast, they found that, while an initial heat-treatment of the parent phase between 150 and 550°C had a negligible effect on the next subsequent A_P (which stayed at the characteristic $\sim 80^\circ\text{C}$ of this alloy³²), successive transformation cycles between -20 and 120°C caused the A_P of such heat-treated material to rise by between 3 and 5°C , with the largest increase associated with the highest initial heat-treatment temperature. The effect saturated at about 20 cycles after which no further increase in A_P occurred. Generally, if A_P increases it may be deduced that the austenite phase has become *less* stable relative to the martensite phase. However, the aging of the parent phase between 150 and 550°C can only have *reduced* its energy, by causing it to move closer

to its equilibrium degree of order and vacancy concentration at the heat treatment temperatures. Decomposition of the β -parent phase can also be ruled out as an explanation for the increase in A_P because (1) there was no change in the first A_P after the high temperature heat treatment, irrespective of whether the heat treatment temperature was 150 or 550°C, (2) the increase in A_P with succeeding cycles of transformation saturated after about 20 cycles, (3) neither diffraction nor microscopy studies have shown evidence that the $Au_7Cu_5Al_4$ β -phase decomposes in this temperature range. Finally, Urbano *et al.* themselves concluded that the high temperature annealing treatments had very little effect on any subsequent SC-SRO –driven aging of the *martensite* phase. Therefore, the mechanism by which aging in the high temperature parent-phase effected the A_P remains unknown in $Au_7Cu_5Al_4$.

In the present work we examine the effects of aging the parent phase in more detail and, after confirming the previously mentioned results of Urbano *et al.*, we show that aging the parent phase at temperatures *lower* than 140°C provides a surprisingly strong *depressing* effect on the subsequent A_P . From the available evidence we conclude that such lower temperature heat-treatments are associated with elastic re-arrangement and migration of the laths in the parent phase, a process that can only occur within a relatively narrow window of temperatures.

Experimental

Samples of alloy were prepared from the pure elements by rapid melting in a muffle furnace in a preheated crucible, or by the re-melting of alloy using an oxy-acetylene flame, or by melting under argon in an arc furnace. The solidus and liquidus of this alloy are in the vicinity of 730 to 800°C respectively^{14, 17} and, at its nominal stoichiometry $Au_7Cu_5Al_4$, it has an *e/a* ratio of 1.48. Samples were weighed out to 6 wt.% Al but the final aluminium content was shown to be around 5.8 wt.% by both wet chemical determination and by SEM-EDS. This composition corresponds to 43.5 at.% Au,

32.3 at.% Cu and 24.2 at.% Al. The samples were annealed at 700°C to convert them into β -phase, followed by quenching into iced brine. Differential scanning calorimetry (DSC) analyses were performed using a Thermal Analysis DSC 2920 with a ramp rate of 10°C/min. Samples were also pulverised in a ring-mill for diffraction studies, and then annealed at 500°C for 3 hours to remove strain. Powder diffraction was undertaken at the Australian Synchrotron on spinning 0.3 mm capillaries filled with Au₇Cu₅Al₄ powder ramped between room temperature and 700 °C. Synchrotron data were collected from a LaB₆ Standard (NIST 660a) to accurately calibrate the wavelength and determine the instrument contributions to the observed line profiles. Samples were analysed at an incident wavelengths of $1.12715 \pm 0.00001 \text{ \AA}$ (October 2008) or $1.15970 \pm 0.00001 \text{ \AA}$ (August 2009). X-ray patterns of bulk samples were obtained on laboratory machines using either Cu-K α or Mo-K α radiation. Due to the large grain size of the bulk material, the X-ray diffraction patterns of these latter samples were strongly effected by texture.

Diffraction data was also collected using 1.6639 \AA neutron radiation on the Medium Resolution Powder Diffractometer of the former HIFAR reactor of the Australian Nuclear Science and Technology Organisation. Neutron diffraction has the advantage of sampling a far larger volume of material than XRD but in this case the samples were not spun, thus accentuating any changes they might undergo in terms of preferred orientation. A technical glitch during this experiment caused the furnace ramp up to abort and, in addition, direct temperature measurements to fail. Fortunately, an estimate of the average temperature experienced by the *parent phase* of the sample during a recording interval could be recovered from its known correlation of lattice parameter and temperature

$$^{\circ}\text{C} \approx \frac{d - 6.1758}{1.1618 \times 10^{-4}}$$

where d is the lattice parameter in \AA (Cortie *et al.* submitted). This calculation was not possible for the martensitic samples. The $M \rightarrow P$ and $P \rightarrow M$ transformation temperatures obtained from the

neutron scans and the empirical correlation mentioned were $\sim 70^\circ\text{C}$ and $\sim 20^\circ\text{C}$ respectively, which are within the expected range for this alloy.

Finally, samples of $\text{Au}_7\text{Cu}_5\text{Al}_4$ that had been through the SMA transformation several times in the past, but then converted to martensite and aged at room temperature for seven years, were soaked at temperatures between 60 and 450°C and scanned in a differential scanning calorimeter in order to determine the effect (if any) of aging the parent phase. Depending on context we report either austenite or martensite start temperatures (A_S or M_S), finish temperatures (A_F and M_F), the temperature at which peak rate of transformation occurred (A_P or M_P), or transformation enthalpies (ΔH_A or ΔH_M). The first measured transformation of these samples was obviously the reverse transformation from martensite to austenite (with associated parameters designated here as A_{P1} or ΔH_{A1}), followed by aging of some kind in the parent phase state, followed by M_{P1} or ΔH_{M1} , then A_{P2} and ΔH_{A2} , and so on, with A_{Pn} for example being associated with the n^{th} thermo-elastic cycle. Note that to heat-treat the *parent* phase at temperatures *below* the A_S we had to first take samples up *past* the A_F , then cool them to the aging temperature (which must still of course be above the M_S to avoid reversion to martensite).

Results

The effect of parent phase heat treatment temperature on a *subsequent* thermo-elastic cycle (M_{P1} then A_{P2}) is shown in Figure 1. For reference, the A_{P1} temperature (76.9°C , $s=1.2^\circ\text{C}$, $n=21$ where s and n are standard deviation and sample size respectively) and ΔH_{A1} enthalpy (1.49 J/g , $s=0.27\text{ J/g}$, $n=20$) preceding the heat treatment are shown as dashed lines. The previous observations in the literature^{22, 32} concerning heat treatments at 150°C and above are confirmed and, furthermore, the A_{P1} value in the present work was not significantly different from the A_P values that had been determined several years before, in the same samples²². This indicated that a nearly a decade of aging at room

temperature did not cause any problematic stabilisation of the martensite, which is a technologically useful result. Annealing between 150 and 450°C caused a small increase in the A_{P2} , to 79.7°C ($s=1.0^\circ\text{C}$, $n=10$), a temperature statistically identical to that reported by Urbano *et al.* ($A_P=80.5^\circ\text{C}$, $s=0.8^\circ\text{C}$, $n=18$)³². The M_{P1} temperature was 18.2°C ($s=6.7^\circ\text{C}$, $n=20$), which is also effectively the same as the 21.6°C ($s=4.5^\circ\text{C}$, $n=18$) reported by Urbano *et al.* The average of the ΔH_{M1} enthalpies was 2.92 J/g ($s=0.91$ J/g, $n=20$). In some other SMAs, such as Cu-Zn, Cu-Al-Ni, Cu-Zn-Al and β -bronze, annealing in this temperature range would cause solid-state decomposition of the β -phase^{3, 9-12} (with a large attendant change in A_P) but this has not been observed in $\text{Au}_7\text{Cu}_5\text{Al}_4$, which appears to be an example of a 'stable' SMA parent phase.

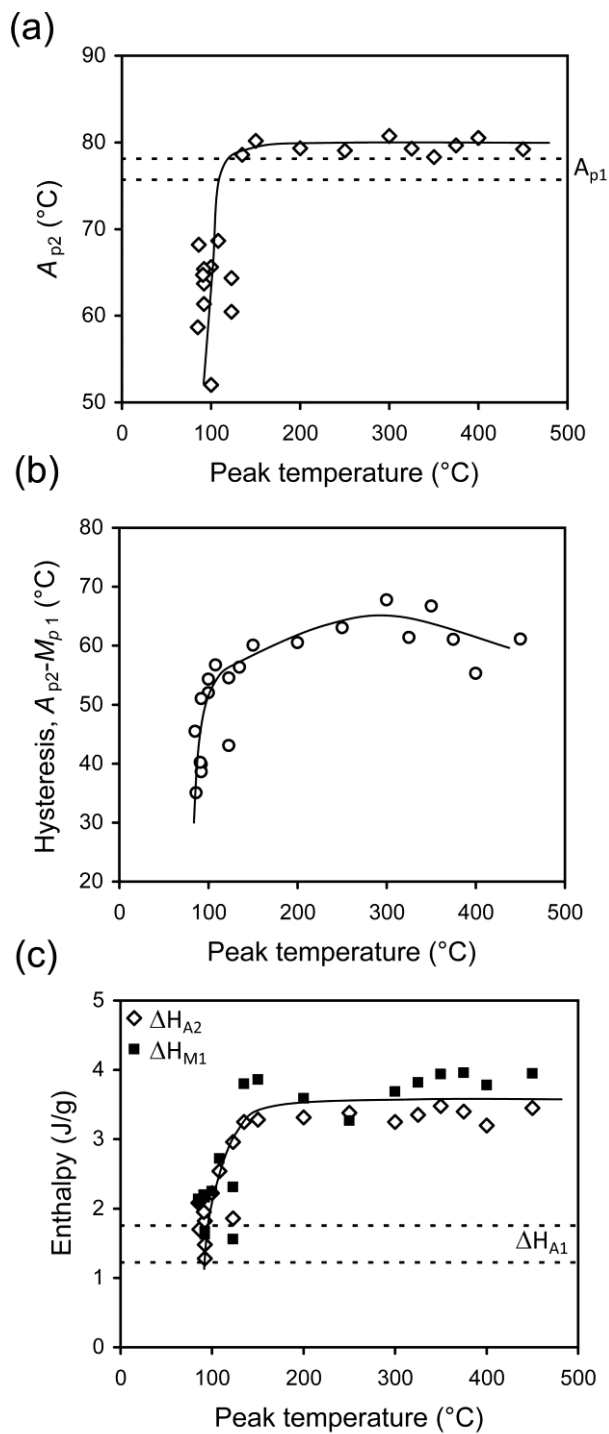


Figure 1. Effect of parent-phase heat treatment on the characteristics of a subsequent thermo-elastic cycle, a. A_p , b. hysteresis, c. enthalpy. Trend lines are drawn merely to guide the eye.

Surprisingly, however, there was a significant *drop* in the A_{P2} when the parent phase of these samples was aged at or cycled to temperatures *below* 140°C, a phenomenon on which the balance of

the present paper is focussed. There is another aspect of Figure 1 also worth noting. This is that the hysteresis ($A_{P2}-M_{P1}$) in the transformation was strongly decreased for the low temperature heat treatments, Figure 1(b). Since the magnitude of the hysteresis is correlated with accumulated plastic strain^{6, 8}, it can be deduced that the high temperature treatments had the net effect of irreversibly ‘locking’ in previous transformation strains. This is also reflected in the higher transformation enthalpies that are associated subsequently with material that had been aged at $>140^{\circ}\text{C}$, Figure 1(c).

Furthermore, we found that repeated thermo-elastic cycling with turn-around temperatures a few degrees higher than A_F , could accentuate the depression in A_{P2} , Figure 2(a). It is evident that the A_{Pn} can be depressed by as much as 20°C by this process. This depressed A_{P2} was not permanent however, and aging at room temperature for 18 hours (dotted line and arrow in Figure 2) caused it to increase back towards the A_{P1} starting value. After several days aging, the A_{P1} temperature of all specimens had reverted to $\sim 80^{\circ}\text{C}$. This systematic decrease in A_P on cycling and on *low temperature* heat treatment ($<140^{\circ}\text{C}$) represents a completely opposite phenomenon to the increase found by Urbano *et al.* for high temperature heat treatments ($>140^{\circ}\text{C}$) and is evidently caused by a different mechanism. The effect on M_P , Figure 2(a), is however surprisingly variable, depressing it in the case of two samples (S19 and S20) and leaving it unchanged in the case of two others (S21 and S22). Evidently, the size, number and orientation of the individual β -phase crystals on these small samples exerts an effect on elastic constraint and hence, apparently, on M_P . Interestingly, in the case of TiNi, repeated cycling is reported to initially decrease M_P ⁷ but later to increase it⁸, so these inconsistencies appear to be relatively common in SMAs⁶.

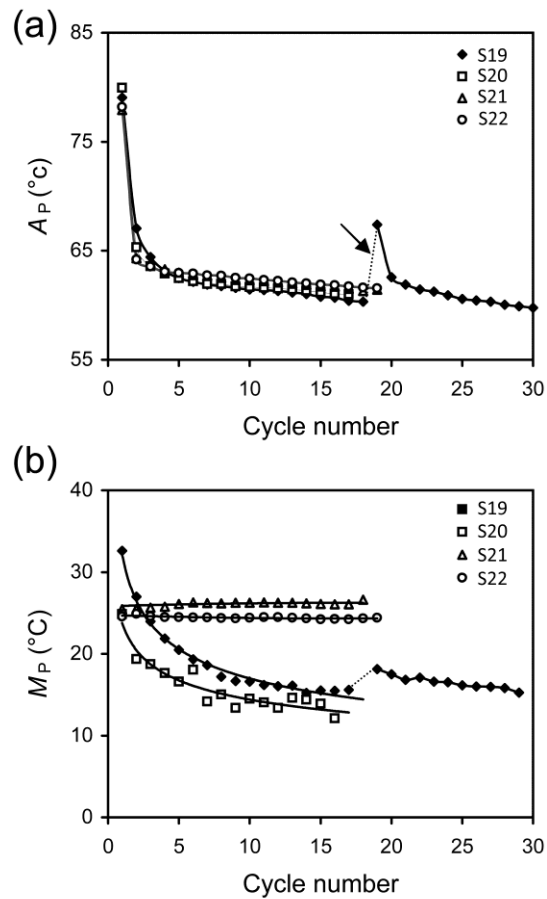


Figure 2. Effect of low temperature cycles on the M_{S_n} and $A_{P_{n+1}}$ temperatures. Samples shown were cycled just past their A_F before immediately cooling again. The arrow and dotted line indicates the effect of 18 hours of aging at room temperature on sample S19.

The time-dependence of these effects was also examined, using a second disk of starting material. It can be seen that the effect of prolonged aging at 90°C is to further strongly depress the subsequent M_{P1} and A_{P2} , Figure 3.

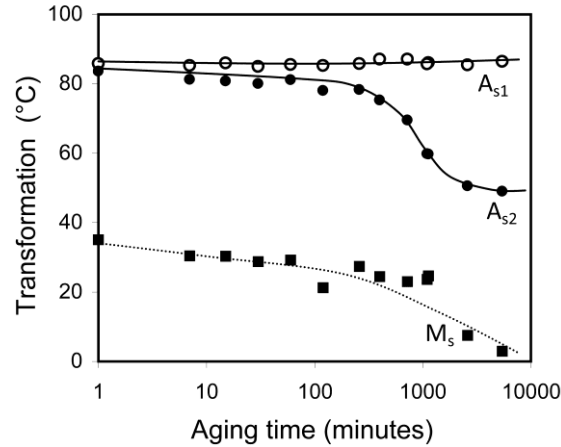


Figure 3. Effect of prolonged aging at 90°C on the temperature of the first succeeding martensite transformation (M_s) and the first subsequent reversion to austenite (A_{s2}). The austenite temperature prior to the aging treatment (A_{s1}) is also shown for reference.

Clearly, the effect of the heat treatments of the parent phase at <140°C has been either to stabilize the austenite relative to the martensite or, conversely but equivalently, to destabilize the martensite relative to the austenite. In either case, the net effect would be to lower the A_P and M_P . The M_P or M_s was generally depressed by these heat treatments, but is in a similar range as the M_P reported by Urbano *et al.*³².

We initially supposed that some structural change was occurring in the parent phase when aged in the low-temperature regime so we ran an *in situ* synchrotron aging tests of the parent phase in the 70 to 140°C range. In Figure 4(a) we show a typical diffraction pattern, and in Figure 4(b) the integrated peak areas obtained when the sample of (a) was slowly ramped through the A_P to about 95°C. The data shown corresponds to 64 minutes of aging in the parent phase condition. The results of a six hour aging treatment are shown in Figure 4(c), obtained in the same sample, but after it had been taken to 680°C and back down again (note that in this case we first took the sample to 140°C to ensure that it was well past the A_F so that there could be no possibility of any martensite remaining. There was no significant change in the X-ray patterns of these spinning samples. To the extent that

any small changes did occur, they can be attributed to some shifting of the contents of the quartz capillary which would have imparted a small degree of texture to the sample due to the relatively small number of particles present. Importantly, the heights of the $\{111\}$ and $\{311\}$ peaks, which in this material indicates ternary ordering of the $L2_1$ type, remained unchanged over these aging treatments. Clearly aging at these temperatures does not cause ordering, disordering or precipitation of second phases.

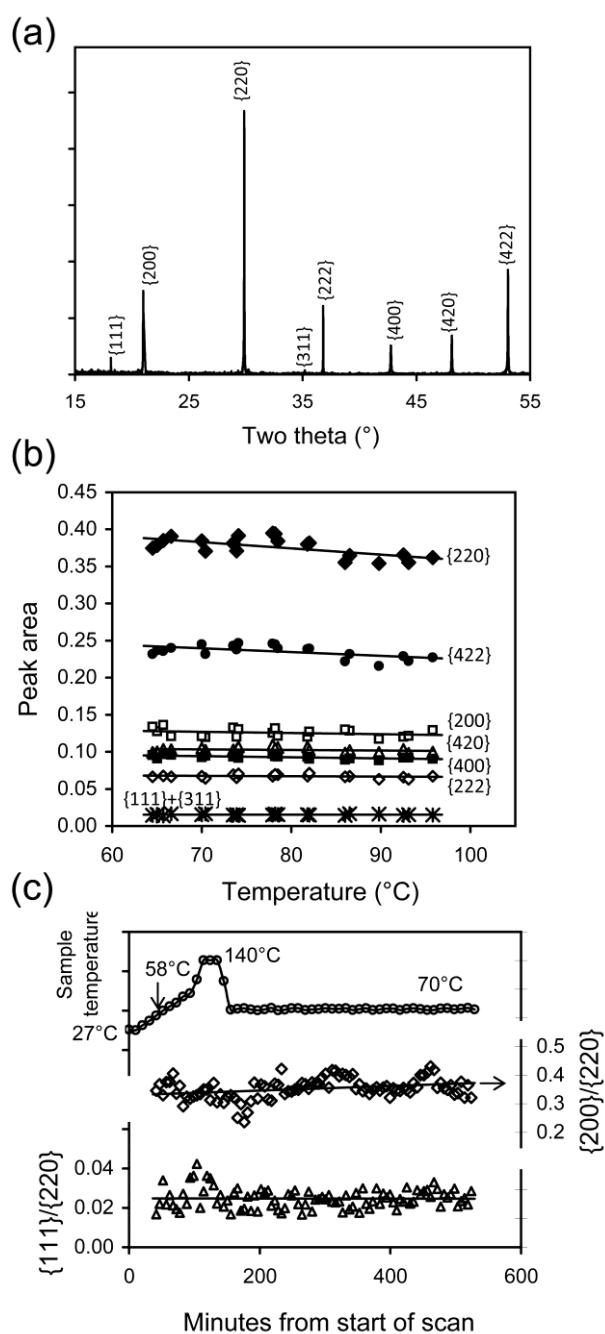


Figure 4. X-ray diffraction patterns of freshly-made parent phase. (a) Complete pattern taken a minute or two after transformation during an up-scan, nominal temperature 70°C, $\lambda=1.12715 \text{ \AA}$. (b) Integrated peak areas of peaks generated by fundamental bcc lattice (filled symbols), B2-ordering (open symbols) and sum of {111} and {311} peak areas due ternary ordering (crosses). (c) Ratio of selected {200} (B2) and {111} ($L2_1$) peak areas to fundamental {220} peak area measured during a later, six hour aging treatment. Note, these samples were spun during measurement to reduce texture effects.

The neutron diffraction patterns of the static polycrystalline sample showed considerable texture and, for example, lacked the expected {400} peak. Furthermore, they underwent a significant change in peak intensities during aging in the parent phase condition, Figure 5. These changes must have been caused by movement of domain boundaries, with consequent effects on the intensity of individual diffraction peaks in these large-grained bulk samples. Note that the {220} and {440} intensities maintained their relative proportions to one another, as is required if the observed changes were due to adjustments in texture, due to the geometric relationship between these two planes. Clearly, although the average crystal structure does not change when parent phase is aged at low temperatures, other changes do occur which can cause movement of domain walls, and hence generate a changed crystallographic texture. Little further change occurred after about 10 hours.

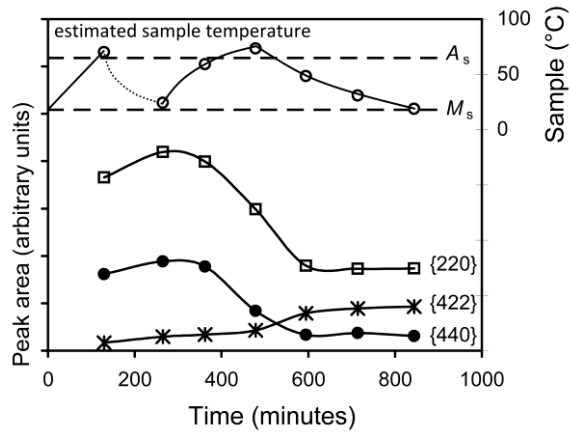


Figure 5. Neutron diffraction data of freshly-made parent phase, showing changes in relative proportions of selected peaks. Note, these samples were statically mounted and hence changes in time-dependent changes in average texture caused the changes in the areas of individual peaks. The approximate temperature profile experienced by the sample is also shown (see Experimental for explanation).

The neutron diffraction experiments also confirmed that the $M \rightarrow P$, and $P \rightarrow M$ transformations, were as expected, first-order in nature, as can be seen by the disappearance of the peaks of the transforming phase and the corresponding appearance of the peaks of the product phase, Figure 6. There is no evidence for the presence of an intermediate phase in either transformation, nor did the synchrotron or neutron patterns contain any evidence for the precipitation of any other phases.

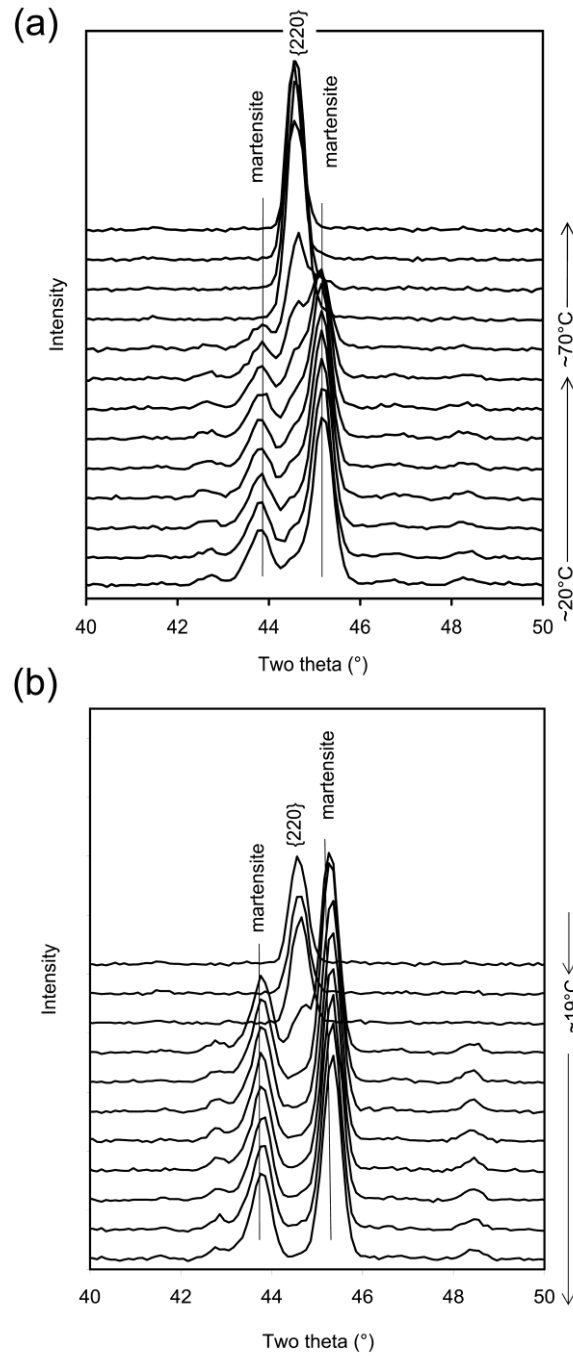


Figure 6. Successive neutron diffraction patterns showing (a) reversion of martensite to parent phase at approximately 70°C, and (b) transformation of parent phase to martensite at approximately 20°C.

Careful examination of the phase transformation on a polished disk mounted on the stage of an optical microscope equipped with Nomarski interference and which was heated and cooled *in situ*, provided direct evidence for changes in lath morphology. In Figure 7, for example, we show the

microstructure observed when cooling the sample from 88°C (*ie.* a few °C above the A_F). Re-arrangements of parent lath morphology occurred at 76, 69 and 61°C as the sample *cooled*. These changes are indicated by arrows in the figure, and they occurred well above the M_S so cannot be due to formation of martensite. The only possible explanation in this case is that they are due to elastically-driven and thermally-activated re-arrangements of the parent phase laths.

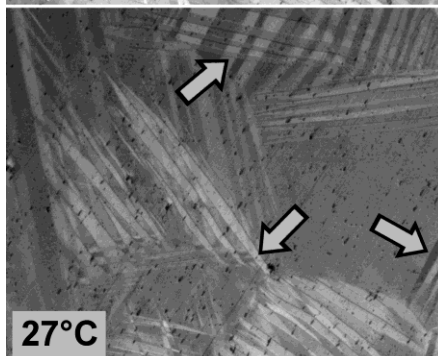
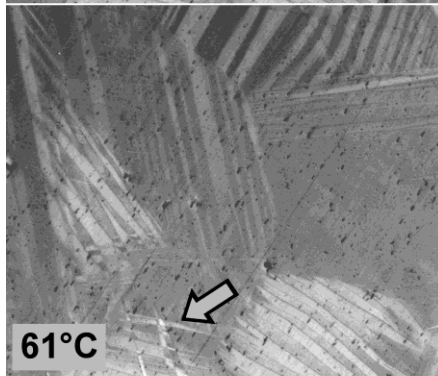
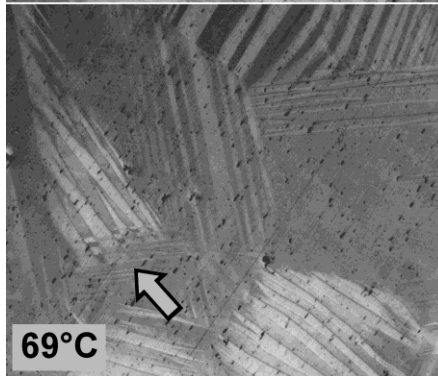
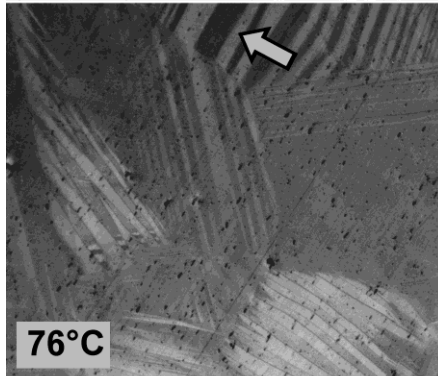
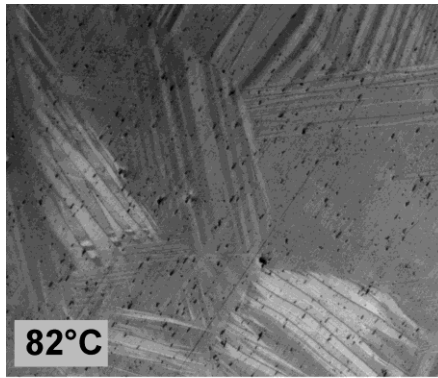


Figure 7. Formation of new laths in the parent phase of $\text{Au}_7\text{Cu}_5\text{Al}_4$ as it *cooled* from 88°C , imaged on an optical microscope.

4. Discussion

Five principle mechanisms for aging were mentioned in the Introduction. The question here is : which of these can explain the *elevation* of A_p after high temperature aging of the parent phase and its *depression* after low temperature aging and low temperature cycling?

The SC-SRO phenomenon can occur during aging of martensite, is readily reversible, and causes the elevation of A_s known as ‘martensite stabilization’. The change occurs without any detectable change in overall lattice occupancies and is due to extremely short-range interchange of atoms on the same sub-lattice, driven by the fact that the chemical ordering inherited by the martensite from its parent phase does not conform perfectly with the lower crystallographic symmetry of the martensite³³. Cycling such stabilized martensite back through the parent phase restores the atomic occupancies to their cubic configuration and resets the martensite to its un-stabilized form. If the SC-SRO mechanism is invoked here and it is assumed that A_p 's of 60°C and 80°C correspond respectively to the transformation of fresh and stabilized martensite to parent phase, then the effect of the high temperature treatment should also have been to lower A_p to 60°C , rather than to raise it to the $\sim 83^\circ\text{C}$ observed. In addition, the SC-SRO effect is reportedly much stronger in quenched than in well-annealed material³, so is expected to be absent in those samples that had been aged in the higher temperature range. Therefore, the SC-SRO effect cannot explain the phenomena observed here.

An alternative explanation invokes the role of anti-site defects and transformation-induced dislocations. It is reasonable to assume that well-aged martensite will be effected by SC-SRO, and that these will stabilise the martensite. Suppose that, in this condition, the A_p is about 80°C .

However, when such material is taken through the reverse transformation, the parent phase will inherit a population of anti-site defects and additional new defects and dislocations will likely be generated by residual non-conservative processes. These defects would certainly be annealed out if the sample is heated to $> 140^{\circ}\text{C}$. However, if the parent phase is cooled back to martensite before these defects can be removed, and if the shape memory reversion is not geometrically perfect, then the resulting martensite will form with a significantly increased content of point defects compared to the previous cycle. In this explanation, the new martensite will have been thereby de-stabilised relative to both the parent phase and normal, well-formed, martensite, and so a subsequent A_P will be reduced. Nevertheless, a day or two's aging at room temperature should be all that is required in this alloy to restore the atoms to the appropriate sites and raise the A_P back to 80°C . The problem with this mechanism is that it predicts that the biggest depression in A_P should follow the minimum (*ie.* shortest and coolest) aging treatment. This is at variance with the time-dependent development of the effect seen in Figure 3. Also, the A_P for martensite freshly formed from well-aged parent phase and that of well-aged martensite of any kind have been observed to be similar ($\sim 80^{\circ}\text{C}$), even though they should have rather different defect populations. Therefore, this cannot be the explanation either.

Next we consider aging due to the elimination of quenched-in vacancies. This is an irreversible thermally-activated process and occurs to a far greater degree in the parent phase than in martensite for purely kinetic reasons^{4,5}. It appears that a high density of vacancies and defects can inhibit the martensitic transformation and lower M_s and for this reason the first thermo-elastic cycle of freshly cast SMAs is usually atypical and often poorly developed²⁷. This effect is removed by a short aging treatment in the parent phase at a temperature some tens of degrees above the A_s . Application of this mechanism to the present phenomenon requires that the starting material contain an appreciable concentration of vacancies, and that the effect of the high temperature heat treatments is to remove these and position A_P at an equilibrium value of $\sim 83^{\circ}\text{C}$. The low temperature parent phase

treatments, in contrast, would not remove the excess vacancies but could eliminate the changes introduced by SC-SRO. Hence the low temperature treatments would lower the A_P to the value typical for the particular vacancy concentration present. If this was the case, then further low-temperature cycling of material that had previously received the high temperature treatment would not lower A_P (which is not the case) while room temperature aging of material that had only received the low-temperature treatment would move A_P back towards $\sim 80^\circ\text{C}$ (which was observed to occur, Figure 2(a)).

Next we consider the possible role of accumulated elastic stresses in either parent or martensite phase and the effect this might have on lath configuration. Generally, elastic stresses generated by one transformation facilitate the subsequent reverse transformation, thereby decreasing the hysteresis between A_S and M_S ^{6, 8}. Conversely, relaxation of the elastic stresses, by domain migration, for example, must retard the reverse transformations and increase the hysteresis⁸. These factors can neatly explain the observed data as follows: high-temperature heat-treatments of the parent phase eliminate elastic strain, therefore not only is the M_S depressed but the martensite thus formed starts with the minimum possible level of new elastic strain. This inhibits the subsequent reverse transformation to parent phase and increases A_P to $\sim 83^\circ\text{C}$. In contrast, low temperature heat treatments of the parent phase allow the parent phase laths to migrate to temporarily form a sub-structure with lower elastic energy. This structure is appropriate to the cubic symmetry of the parent phase but conversion of it to back to martensite will produce a higher than normal degree of elastic strain in the martensite (which now contains both the normal elastic strain energy of its own laths and the ‘alien’ elastic configuration inherited from the stabilized parent-phase sub-structure). This effect will endure until SC-SRO-driven changes in the martensite relax the elastic stresses. This mechanism requires that time-dependent changes in lath morphology be observed in the parent and martensite phases. This is the case, Figure 3.

Finally, precipitation of second phases is also possible in some systems. It arises because the β -phase generally has a V-shaped phase field on its isopleths, so there is a temperature below which, under equilibrium conditions, the β will decompose, e.g. by the reactions $\beta \rightarrow \alpha + \gamma$ or $\beta \rightarrow \alpha + \delta$. This is more commonly encountered during the aging of parent phase rather than in martensite, due to this process requiring diffusive mass transfer and hence higher temperatures. Besides generating a second phase, such a reaction will change the transformation temperatures of the $M \leftrightarrow A$ reaction, by changing the composition of the parent phase or even destroying it, or, possibly, by generating precipitates that pin the interfaces of the laths. Decomposition has a variable effect, and has been generally but not exclusively reported to depress M_s or A_p ^{12, 34-37}. It is clear, however, that decomposition of the β -phase is not an explanation of the present phenomena as no sign of this occurrence was evident in the synchrotron or neutron diffraction patterns. Additional chemical ordering during the low-temperature heat treatment of the parent phase (which would also have changed the relative stability of parent and martensite phases) can similarly be excluded by consideration of the relevant diffraction patterns.

5. Conclusions

We have established that well-ordered forms of the martensite and parent phase in the $\text{Au}_7\text{Cu}_5\text{Al}_4$ alloy are stable and resistant to both decomposition and stabilization, and exhibit consistent transformation temperatures. This is an attractive property for a shape memory system. On the other hand, samples that have only experienced a low-temperature, aging treatment in the parent phase will temporarily have a suppressed A_p . We propose that this is due to the elastic stresses in the parent phase laths of such samples having been reduced by a reversible, time-dependent, process of domain migration. The result is that any martensite produced from such elastically relaxed parent phase

inherits a lath structure and elastic strains that facilitate a reversion to parent phase (and therefore this lowers the subsequent A_P to $\sim 60^\circ\text{C}$). However, this inherited configuration ages and relaxes over the course of a few days at room temperature and the A_P is thereby restored to its usual level. The time-dependent changes in the martensite at room temperature are probably due to a combination of SC-SRO and lath migration. In contrast, when parent phase is heated $> 140^\circ\text{C}$ the elastic stresses are annealed out. Martensite produced from such parent phase is more stable overall, and the associated A_P is $\sim 80^\circ\text{C}$.

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