

Influence of Heat Treatment on the Mechanical Behaviour of a NiTi Alloy

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Measurements of the effect of heat treatment following cold work on the yield and shape memory behaviour in a NiTi alloy are reported. Tensile behaviour is found to depend on test temperature and initial structure as well as annealing temperature. Minimum values of stress required for stress induced martensite, martensite reorientation and parent phase yield were found to be associated with the as-recrystallized structure. Measurements of reversion and permanent strains were found to depend on applied stress.

KEY WORDS: shape memory alloy; NiTi alloy; heat treatment; martensitic transformation; stress-induced transformation; tensile testing; thermal cycling.

1. Introduction

The mechanical properties of NiTi shape memory alloys, particularly tensile behaviour, have attracted considerable interest in recent years.¹⁻⁴⁾ Stress-strain behaviour resulting from stress induced martensite (SIM), martensite reorientation (MR) and the distinct stage of yielding associated with the *R* phase is well established and understood. The effects of test temperature,⁵⁻⁹⁾ alloy composition^{8,9)} and heat treatment^{5,9,10)} on mechanical properties and shape memory behaviour have also been extensively studied. With respect to heat treatment, many studies have been concerned with the ageing behaviour in alloys containing excess Ni. The influence of heat treatment temperature on pseudoelastic and shape memory behaviour has been examined, however, a full understanding of the effect of heat treatment on mechanical behaviour is yet to be achieved.

Recent studies¹¹⁾ have shown that the two way memory (TWM) behaviour in NiTi alloys is dependent on heat treatment. The TWM has been shown to depend on transformation behaviour, with a single stage martensitic transformation being required for the development of a significant TWM effect. For alloys containing near stoichiometric compositions a minimum heat treatment temperature is required to avoid the two-stage parent $\rightarrow R$ phase \rightarrow martensite transformation on cooling.¹²⁾ However, even in specimens heat treated to give a single martensitic transformation the TWM training characteristics seem to be still affected by heat treatment. In evaluating the TWM behaviour it became apparent that a systematic study of the effect of heat treatment on mechanical behaviour was required. This study is focused on the tensile behaviour of a NiTi alloy annealed at various temperatures following cold work.

Another mechanical property of importance to TWM training is the reversion behaviour during heating. A number of investigations have been carried

out to evaluate the reversion characteristics in constrained specimens.^{7,13-15)} Apart from the knowledge that the reversion stress increases with increasing prior strain and temperature, little has been understood about the reversion process. A vital point concerning both TWM training behaviour and practical application is the maximum stress that can be withstood during reversion rather than the stress that can be achieved under a particular set of testing conditions. This study also reports the results of initial measurements of the effect of applied stress on the reversion strain.

2. Experimental Procedure

The NiTi alloy used in this study was a commercial alloy, of nominal composition Ti-50.2at%Ni, supplied by the Shanghai Iron and Steel Research Institute. The as-received material was cold rolled to give a 50 % reduction in cross-sectional area, giving wire specimens of square cross-section 0.87×0.87 mm. The specimens were then annealed for 1.8 ks at various temperatures between 670 and 1 200 K, followed by air cooling to room temperature. Tensile tests were carried out on specimens of 20 mm gauge length using an Instron testing machine. Test temperatures were varied between 263 and 473 K using a stirred liquid temperature bath and appropriate heat transfer fluids. Test temperatures were controlled to within 0.5 K. The reversion tests were carried out on a constant load thermal cycling device which has been described elsewhere.¹¹⁾ Transformation temperatures at zero stress were measured using a Perkin Elmer DSC-4 differential scanning calorimeter.

3. Results and Discussion

3.1. Tensile Behaviour

Typical stress-strain curves obtained in this study over the temperature range from below M_f to above

A_f are shown in Fig. 1. As reported by Miyazaki and Otsuka⁴⁾ and others,^{5,6,16)} the stress-strain behaviour was critically dependent on the structure of the alloy. To ensure an initial single phase structure, specimens tested within the range of transformation hysteresis were either cooled to below M_f prior to testing at temperatures up to A_s to give a fully martensitic structure, or heated to above A_f for tests in the temperature range $A_f > T > M_s$ for 100% R or parent phase structure.

Deformation of the martensite structure initially occurred by reorientation of the martensite plates. As shown in Fig. 1(a), this process was characterised by an initial yield plateau on the stress-strain curve. The horizontal yield plateau is indicative of localisation of the martensite reorientation process into a narrow Luders-type band which propagates along the gauge length of the specimen. Such behaviour was observed in all specimens tested at temperatures up to A_s which were initially cooled to below M_f . On completion of the localised reorientation process, further deformation occurred by elastic/plastic deformation of the oriented martensite variants.

Specimens heat treated at temperatures below 850 K exhibited the R phase (*i.e.*, $T_R > M_s$). Specimens tested in the temperature range $T_R > T > M_s$ exhibited two stage yielding as shown in Fig. 1(b). The initial yielding stage is associated with stress directed reorientation of the R -phase¹⁷⁻¹⁹⁾ via the movement of twinning boundaries^{18,19)} and the second stage with the formation of stress induced martensite.¹⁶⁾ As discussed above, the yield plateau indicates transformation localisation into a discrete band. Such localisation of the SIM transformation has been reported by

Miyazaki *et al.*²⁰⁾

The deformation behaviour of the parent phase was dependent on test temperature and heat treatment. In specimens heat treated such that $T_R > M_s$ two stage yielding associated with stress induced R and martensite respectively occurred over a limited temperature range above T_R . The stress-strain curve was similar to Fig. 1(b), with stress required for stress-induced R phase increasing rapidly with increasing temperature.^{4,16)} At higher temperatures only a single yield plateau associated with SIM occurred when the stress required for stress induced R phase exceeded that for SIM (Fig. 1(c)). Similar yield behaviour has been previously reported by Miyazaki and Otsuka.²¹⁾

In specimens heat treated such that $M_s > T_R$, the yield behaviour of the parent phase also depended on the test temperature. At temperatures near M_s , a horizontal yield plateau was not observed, but rather the formation of SIM required an increasing stress as shown in Fig. 1(d). At higher temperatures a distinct horizontal yield plateau was observed similar to Fig. 1(c). For all heat treatments testing above a critical temperature, T_a , which depended on annealing temperature, resulted in plastic deformation of the parent phase and the initial stage of yielding associated with SIM was no longer observed (Fig. 1(e)).

The effect of test temperature on the yield stress of specimens heat treated at 881 and 975 K is shown in Fig. 2. For both heat treatments separate curves for the martensitic and parent phase structures are given. As discussed previously, initial yielding of the martensite structure proceeds by reorientation of martensite variants and is characterised by a small, negative temperature dependence of the yield stress (region I).

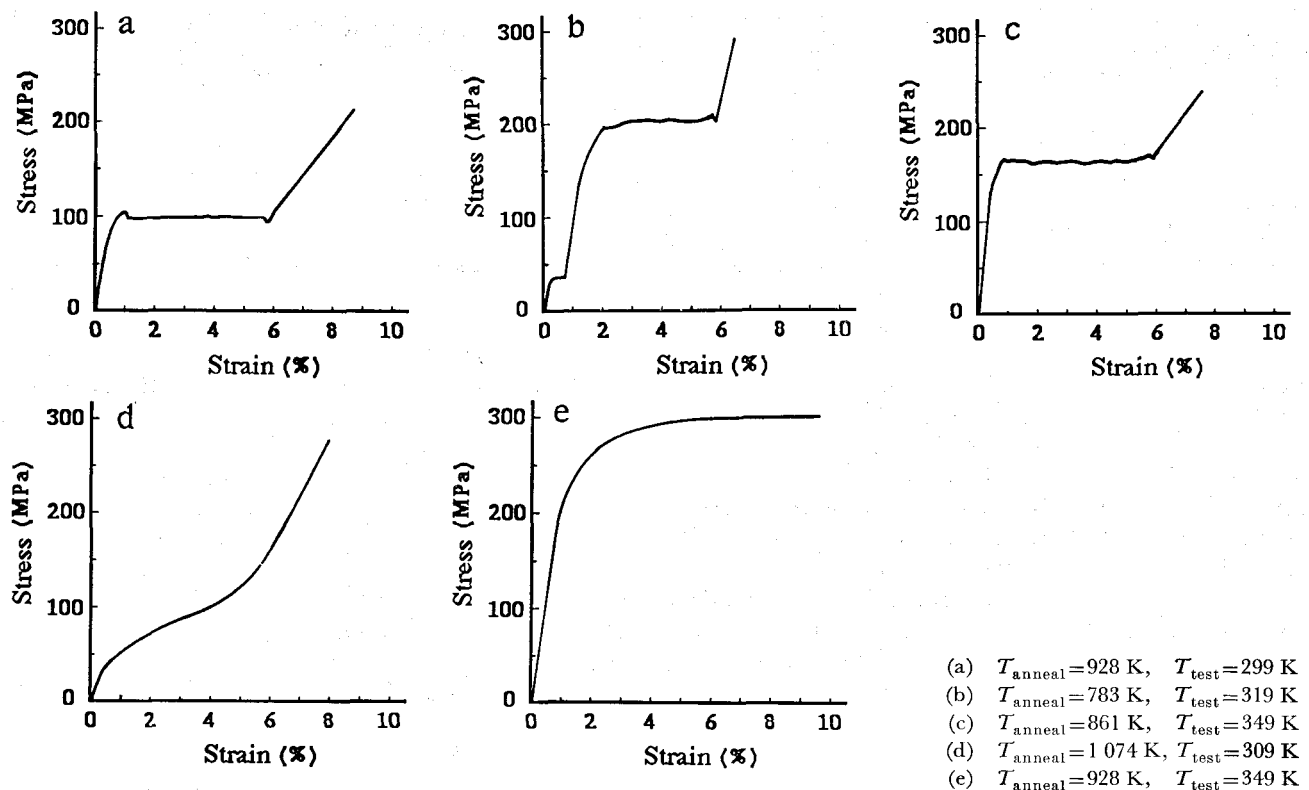


Fig. 1. Effect of test temperature on yield behaviour.

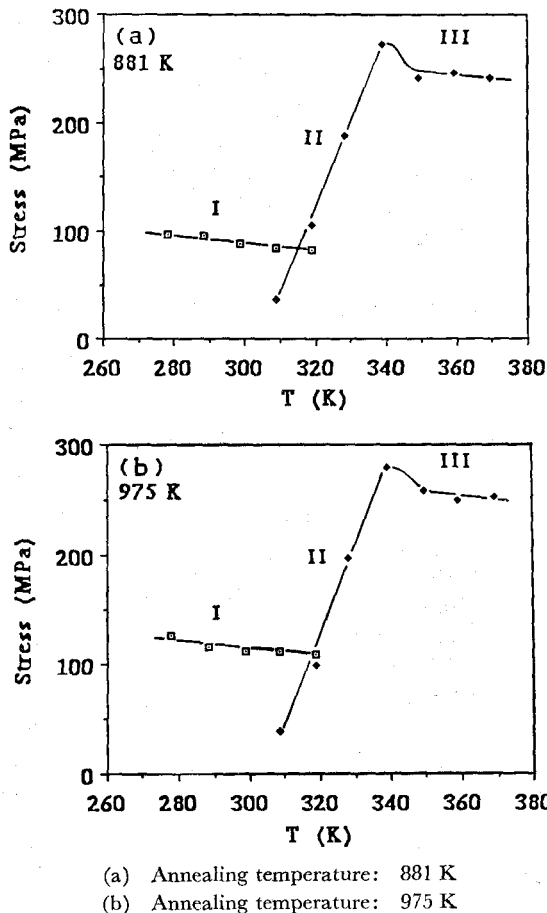
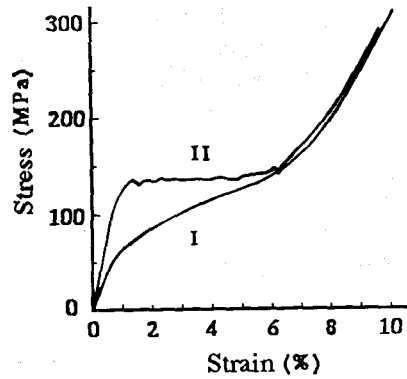


Fig. 2. Yield stress as a function of test temperature.

The yield stress-temperature curves for the parent phase exhibit two distinct regions (II and III) associated with SIM and plastic yielding of the parent phase, respectively. The transition from region II to III occurs when the stress required for SIM exceeds the stress required for slip in the parent phase. The small negative temperature dependence of the yield stress in regions I and III is expected of yielding processes involving twinning and slip, while the temperature dependence in region II follows the Clausius-Clapeyron type relation inherent with SIM.^{22,23} Values of M_s obtained from extrapolation of the curve in region II to zero stress were found to be in excellent agreement with values obtained from DSC measurements.

The processes of martensite reorientation and stress induced martensite are distinctly different, each characterised by a critical stress. Therefore, there is no reason for the curves of regions I and II to join continuously as is often assumed.^{5,8,9} Rather, as shown in Fig. 2, an abrupt increase in yield stress should occur at M_s in specimens cooled from $T > A_f$. Similarly, an abrupt change in yield stress should occur at A_f in specimens initially cooled to below M_s if the stress required for SIM at A_f differs from that required for martensite reorientation.

At a given temperature in the range between M_f and A_f the microstructure and hence mechanical behaviour of a shape memory alloy will not be unique because of the transformation hysteresis between the



I: Specimen cooled from 363 K
II: Specimen heated from 223 K

Fig. 3. Stress-strain curves.

forward and reverse transformations. For example, suppose an alloy has values of M_s and A_s such that $A_s > M_s$. On cooling from a temperature $T > A_f$, the parent phase will be present in the temperature range between A_s and M_s , while the martensite phase will be present in the same temperature range if the specimen is heated from a temperature $T < M_f$. In Fig. 3 stress-strain curves of two specimens heat treated at 1 025 K and tested at the same temperature within the M_s - A_s temperature interval are shown. Specimen I was cooled down to the test temperature of 309 K from $T > A_f$. This specimen yielded at a stress of 39 MPa by the formation of stress induced martensite. Specimen II was initially cooled to 220 K ($T < M_f$) and then heated to the test temperature. This specimen yielded by martensite reorientation at a stress of 96 MPa. It is of interest to note that even though the yield stresses and modes of yielding of the two structures are different, the resulting strains associated with SIM and martensite reorientation are virtually the same.

3.2. Effect of Annealing Temperature

The effect of annealing temperature on the stress required for martensite reorientation, σ_R^M , and yielding of the parent phase, σ_y^P , is shown in Fig. 4. In view of the small temperature dependencies of σ_R^M and σ_y^P in regions I and III, the values shown in Fig. 4 are average values. The effect of annealing temperature on the stress required for SIM is shown in Fig. 5. For all three stresses minimum values were observed after heat treating in the temperature range of 870 to 1 000 K.

The temperature of the stress minimum corresponds well with the recrystallization temperature of this alloy as determined metallographically. At lower annealing temperatures the dislocation structure introduced by cold working is only rearranged by heat treatment, resulting in higher values of internal stress which must be overcome by the applied stress. The degree of recovery decreases with decreasing temperature and therefore the stresses required for slip in the parent phase, reorientation of martensite variants and stress induced martensite all increase with decreasing an-

nealing temperature. The stress required for parent phase slip is increased relative to the stress for SIM, as evidenced by the improvement in pseudoelasticity in alloys annealed at temperatures below 900 K. The M_s temperature also decreased with decreasing annealing temperature, resulting in R phase formation in samples annealed below 850 K.

The increase in σ_R^M , σ_{SIM} and σ_y^P with increasing annealing temperatures above ~ 1000 K is unusual. Apart from the measurements of Saburi *et al.*,⁵⁾ which show increases in σ_R^M and σ_{SIM} on increasing the annealing temperature from 973 to 1273 K and 873 to 1273 K, respectively, there appears to be no systematic studies of the effect of annealing temperature in the range 900 to 1300 K on mechanical properties. Most annealing studies have been concerned with the ageing behaviour of alloys containing excess Ni (>50.7 at%). These studies have shown that ageing of these alloys at 773 K results in the precipitation of a Ni rich phase, resulting in an increase in M_s temperature due to increased Ti in the matrix. The alloy used in this study contained 50.2 at% Ni and the M_s was found to increase with increasing annealing temperature for temperatures below that required for recrystallization ($T \sim 850$ K) and was constant at higher annealing temperatures. Tietze *et al.*²⁴⁾ have reported changes in texture and microstructure in NiTi alloys after annealing at temperatures up to

1320 K, however, the relation between such changes and mechanical behaviour was not examined. Microstructural studies are currently being carried out and will be reported elsewhere.²⁵⁾

3.3. Reversion Behaviour

The effect of stress and heat treatment on the reversion and permanent strains was studied using constant load thermal cycling tests. A typical thermal cycling test is shown in Fig. 6. A specimen was first heated to the starting temperature (above A_f) under zero stress. A load was applied and the specimen was cooled to below M_f , resulting in the formation of SIM. Then the specimen was reheated to above A_f , causing the reverse transformation to occur. As shown in Fig. 6 the reversion strain, ϵ_r , was determined directly from the heating curve. The permanent strain at the end of the cycle, ϵ_p , was obtained after removing the load. The ratio of the reversion strain to the total recoverable strain ($\epsilon_t = \epsilon_f - \epsilon_{pf}$) may be taken as a measure of reversibility or reversion efficiency. In Fig. 7 the ratio ϵ_r/ϵ_t is plotted as a function of applied stress for specimens heat treated at 976 and 1189 K, respectively. It is seen that the reversion efficiency decreases almost linearly with increasing stress from a value of 1 at $\sigma=0$. The specimens heat treated at 1189 K showed a slightly higher reversion efficiency than those heat treated at 976 K.

The permanent strain occurring during the forward transformation on cooling, ϵ_{pf} , was obtained by

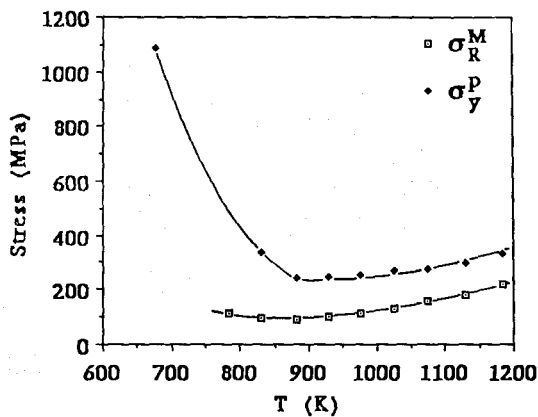


Fig. 4. Effect of annealing temperature on stress for martensite reorientation and parent phase yielding.

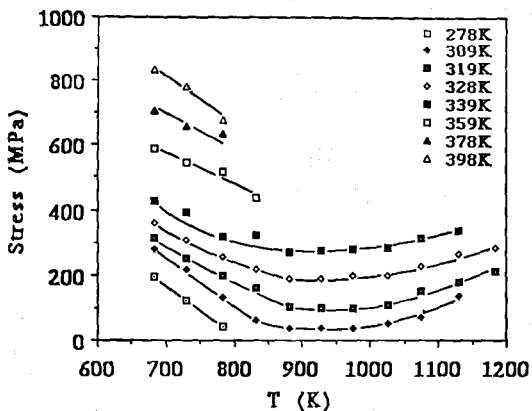
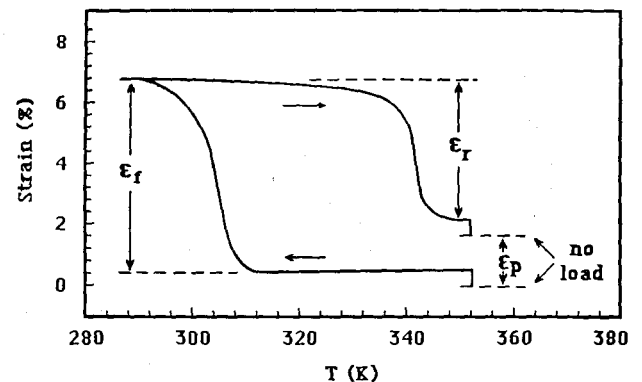


Fig. 5. Effect of annealing temperature on stress for stress-induced martensite at various test temperatures.



$\sigma = 140$ MPa

Fig. 6. Typical strain-temperature curve for thermal cycling test.

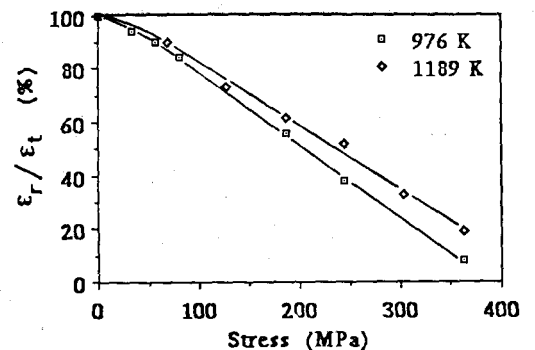


Fig. 7. Effect of stress on reversion efficiency.

removing the load at the end of the cooling cycle and heating under zero load. It was assumed that no permanent strain accompanied the reversion process under zero stress. In Fig. 8 measurements of ϵ_{pf} are plotted as a function of annealing temperature for three values of applied stress. As would be expected the values of ϵ_{pf} increased with increasing stress. Maximum values of ϵ_{pf} occurred for specimens annealed at 976 K, and for annealing temperatures less than, 720 K, $\epsilon_{pf}=0$.

The permanent strain occurring during reversion to the parent phase, ϵ_{pr} , was determined by subtracting the forward strain, ϵ_{pf} , from the total permanent strain at the end of the full cycle, ϵ_p . In these tests the specimens were cooled under the same stress to provide a constant starting condition for the reversion half cycle, and the stress was changed to its new value at the start of heating. The effect of stress on ϵ_{pr} for specimens heat treated at 976 and 1189 K is shown in Fig. 9. In agreement with Fig. 7 specimens heat treated at 1189 K showed a slightly higher resistivity to permanent deformation than those heat treated at 976 K. Also shown in Fig. 9 are the corresponding values of the parent phase yield stress for the three annealing temperatures. Comparison of Figs. 8 and 9 shows that for the same applied stress and annealing temperature the permanent strain occurring during reversion substantially exceeds the permanent strain

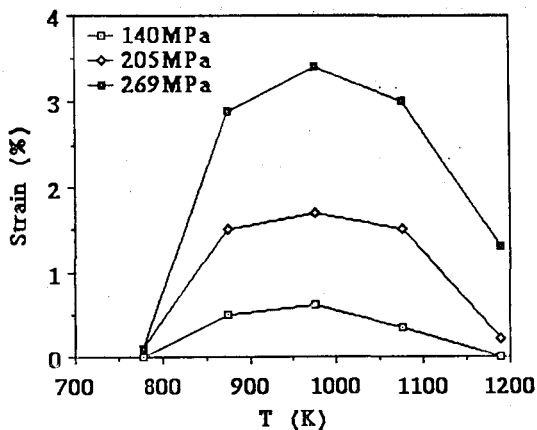


Fig. 8. Effect of annealing temperature and stress on ϵ_{pf} .

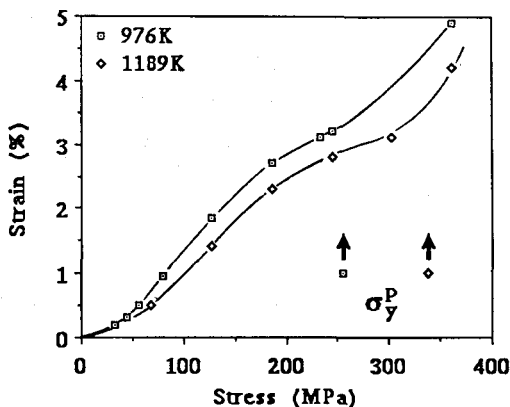


Fig. 9. Effect of stress on ϵ_{pr} for specimens annealed at 976 and 1189 K.

occurring during the forward transformation. Selected values of ϵ_{pf} and ϵ_{pr} as well as reversion strain, ϵ_r , are given in Table 1.

The distribution of permanent strain through the cycle was determined by applying a load through to various stages of the cycle, removing the load and completing the cycle under zero stress. In Fig. 10 the fraction of the total permanent cycle strain is plotted as a function of the fraction of cycle completed. It is evident from Fig. 10 that ϵ_{pf} is uniformly spread over the cooling half cycle. However, the distribution of ϵ_{pr} appears to be somewhat more concentrated near the beginning of the reversion than near the end.

From Fig. 8 it is clear that low annealing temperatures are required to eliminate or minimize the permanent strain accompanying the formation of SIM. For annealing temperatures greater than 770 K significant permanent strains were obtained for applied stress well less than the parent phase yield strength. In these specimens, as shown in Figs. 7 and 9, zero permanent strains were only obtained in the limit of zero applied stress. The development of significant permanent strains at stresses below σ_y^p is indicative of the generation of high local stresses at the martensite/parent phase interface during the transformation. It is apparent that local yielding also occurs in unstressed specimens, but does not result in a net permanent overall strain due to the self accommodating nature of the martensitic transformation. With increasing stress the degree of self accommodation of the martensite plates decreases, and as a consequence ϵ_p increases. The observation that the permanent strain developed during reversion exceeds the permanent strain associated with the forward reaction ($\epsilon_{pf} > \epsilon_{pr}$) implies an additional effect associated with the direction of the transformation. Such behaviour indicates that the local stresses generated during reversion (when the transformation is doing work against the applied

Table 1. Values of reversion and permanent strains.

Annealing temp. (K)	σ (MPa)	ϵ_r (%)	ϵ_{pf} (%)	ϵ_{pr} (%)
976	127	3.8	0.6	1.9
1076	186	3.5	1.5	2.4
1189	245	2.8	1.3	2.8

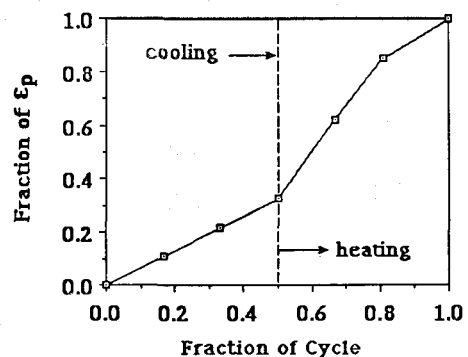


Fig. 10. Distribution of permanent strain over thermal cycle.

stress) exceed the local stresses generated during the forward transformation.

The effect of annealing temperature on the permanent cycle strains is in general agreement with the effect of heat treatment on the parent phase yield stress as discussed in Sec. 3.2. Maximum permanent strains were observed in specimens annealed near the recrystallization temperature. In addition to the measurements reported here, the annealing temperature has also been found to have a significant effect on the TWM developed from constant load thermal cycling.*

4. Conclusions

(1) The yield behaviour of NiTi is dependent on initial structure. In the region of transformation hysteresis ($M_f \sim A_f$) the structure, and hence properties, are not unique to a particular temperature but depend on the prior thermal history of the specimen.

(2) Measurements of the effect of annealing following cold work show that minimum values of the stresses for SIM, martensite reorientation and yielding of the parent phase are exhibited at annealing temperatures near that required for recrystallization. The increase in the characteristic stresses at lower annealing temperatures may be associated with higher internal stresses. The reason for the small increase in the stresses for higher annealing temperatures is yet to be solved.

(3) The recoverable strain accompanying the reversion of martensite to the parent phase decreases approximately linearly with increasing applied stress.

(4) Measurements of permanent strains associated with the formation and reversion of stress induced martensite show that a greater permanent strain accompanies the reversion of martensite to the parent phase rather than *v.v.* Substantial permanent strains were observed for applied stresses well less than the yield stress of the parent phase.

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