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Materiala and Research Society Symposium Proceedings
Vol. 245
"Shape Memory Materials and Phenomena - Fundamental Aspects and Applications"
pp. 159-167

1992

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DIFFUSE YIELD DROP AND SNAP ACTION IN A NI-TI ALLOY

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ABSTRACT

An unusual yield phenomenon is observed in a heavily worked NiTiFe alloy, which leads to *snap action* shape memory and superelasticity. The snap action occurs at extremely high velocities and is accompanied by a loud cracking sound. The cause of the instability is attributed to *penning*, in which martensite growth is halted by having to undergo a reorientation at low angle cell boundaries, which then lowers the resolved shear stress on the martensite plate. Once free of the cell boundary, the plate grows and its strain energy is reduced so that it is able to penetrate subsequent boundaries more easily. This results in a diffuse yield drop, and the said snap action motion.

INTRODUCTION

NiTi alloys are well-known for their two-step martensitic transformation from ordered cubic austenite, to the rhombohedral R-phase, to a monoclinic martensite. Both transformations are thermoelastic and can, under certain circumstances, give rise to shape memory and superelasticity. Iron is often added to equiatomic NiTi alloys in order to suppress the martensitic transformation temperture while maintaining stability and high ductility. The alloy is predominantly used to make fluid fitting couplings for the aerospace and marine industries. In order to develop lighter weight and higher performance components, it is of importance to keep the austenitic strength as high as possible. This is usually accomplished by cold working and then annealing so that the early stages of recovery take place but recrystallization is suppressed. An alternative method of achieving the same result, however, is to work the alloy at a temperature and strain rate which allow the alloy to dynamically recover. In doing so, a fine, well defined substructure is created which offers high strength, high ductility, and as will be shown, a snap action martensitic transformation.

EXPERIMENTAL

The material used in this study was a $Ti_{50}Ni_{47}Fe_3$ alloy prepared by e-beam melting, hot rotary forging and warm swaging some 40% at 500°C, well below the recrystallization temperature of the alloy. The M_s temperature in this condition was measured to be -210°C. All test specimens had a gauge diameter of 6.35 mm and a gauge length of 4 inches. (This unusually long gauge length was chosen to minimize the heat sinking effects of the grips and to obtain as uniform a temperature as possible along the gauge length of the extensometer region.) All tests were conducted in an MTS servohydraulic machine equipped with a programmable convective thermal chamber and an extensometer.

RESULTS

The microstructure can only be discerned using TEM. Figure 1 confirms that the alloy was in fact extensively deformed below the recrystallization temperature of the alloy, but above the temperature at which recovery processes begin. The sub-grain size is typically 1μm, and although there were a large number of dislocations within the sub-grains, most are coalesced into the cell walls. Although it is difficult to verify in a single photograph, observations made while tilting indicate that the cells are in fact uniform in size. The deformation and recovery processes that take place, and the resulting microstructure have been reported in more detail elsewhere [1].

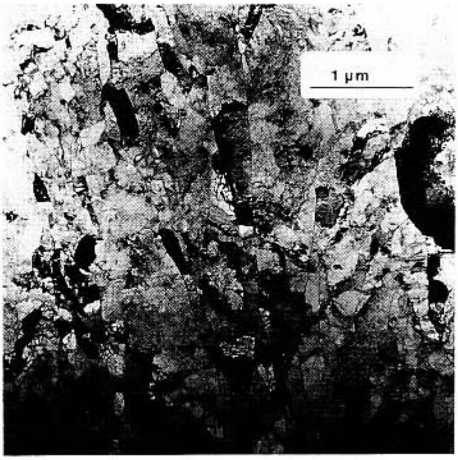


Figure 1: TEM micrograph showing the structure of the subject alloy, with a fine cellular structure of low angle boundaries and dislocation debris within.

The Yield Drop during Loading

Figure 2 represents the tensile behavior of the subject alloy deformed to 9% at -196°C (just above M_s) and then unloaded. It is important to note that the test was conducted in strain control, meaning that the applied strain is monotonically increased, and load is left to vary at will. The curve is shown in engineering units (instead of true) because of the strong Lüders band formation occurring during deformation; this means that the deformation in not uniform, and the conventional definitions and conversion techniques are meaningless.

Figure 2 exhibits several interesting features. Prior to loading, the R-phase is stable. At a stress of S_r, the R-phase variants begin to move, consuming one another until aligned in the way that yields the greatest strain in the tensile direction [2,3]. The strain accommodated by this rearrangement averaged approximately 1.3%. This is somewhat greater than has been reported in the past, but expected considering how far below R_s the test was conducted: it is well-known that the rhombohedral distortion of the R-phase continues to increase after the phase is originally formed, resulting in a steadily increasing shape strain with decreasing temperatures [4].

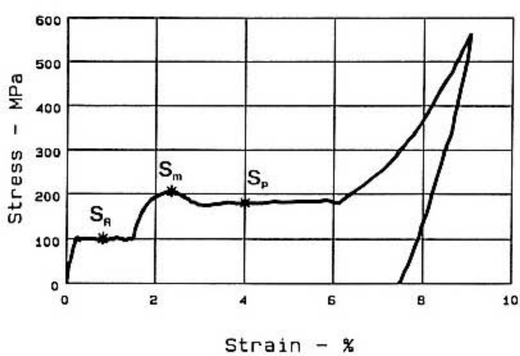


Figure 2: Engineering stress-strain curve of NiTiFe alloy tested in strain control at -196°C

Upon completion of the R-phase reorientation, deformation continues elastically. At the point on the curve marked "S_m", there is a marked, but gradual yield drop, to the plateau stress marked "S_p". This plateau is a result of stress inducing the R-phase-to-martensite transformation. After a total strain of 6%, the structure is 100% martensitic, and the material can only deform elastically, and then eventually through conventional slip mechanisms.

Unlike the familiar Lüders yield found in carbon steels, the yield drop in Figure 2 is symmetrically diffuse, without the serration characteristic of steels. This is a very important attribute of the deformation behavior, and one that clearly requires the rejection of many commonly proposed mechanisms based on pinning arguments. Further, unlike most other yield drops, the material must be deformed some additional 4% before the stress again rises to the magnitude of the peak stress, S_m.

In order to better understand the structure of the material at S_m, a specimen was loaded only to that stress (Figure 3a) then unloaded and heated (Figure 3b). Figure 3b clearly shows a two-stage recovery profile, verifying that the deformation associated with the first plateau is in fact due to the R-phase (recovering at -40°C in Figure 3a). The deformation occurring just before the peak is reached, however, is recovered at a much lower temperature, verifying that this deformation is in fact due entirely to stress induced martensite. This also verifies that the yield drop is not caused by difficulties in nucleating martensite; Figure 3b clearly shows that martensite is present, yet the stress has not yet reached its peak. Based upon the strain recovered, one can estimate the volume fraction of martensite present at the peak of the yield phenomenon to be 10-15%.

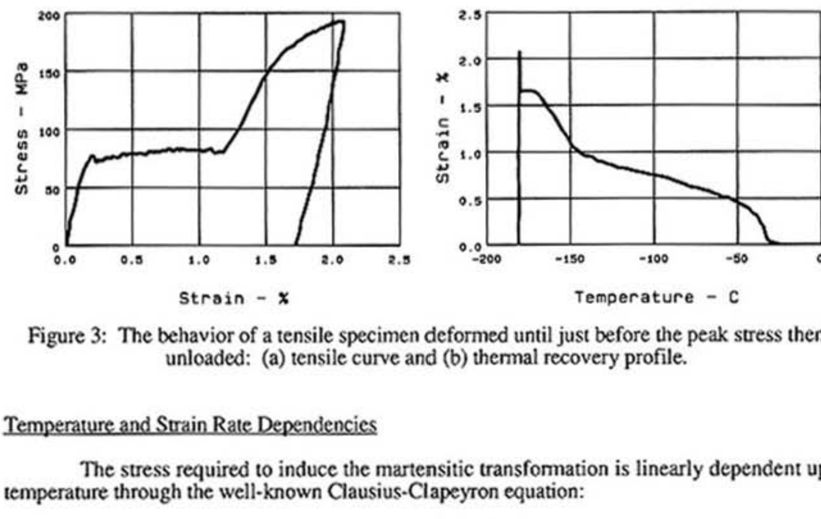


Figure 3: The behavior of a tensile specimen deformed until just before the peak stress then unloaded: (a) tensile curve and (b) thermal recovery profile.

<u>Temperature and Strain Rate Dependencies</u>

The stress required to induce the martensitic transformation is linearly dependent upon temperature through the well-known Clausius-Clapeyron equation:

$$d\sigma/dT = -\Delta H/T\Delta\varepsilon \qquad (1)$$

Figure 4 shows the temperature dependencies of the three stresses marked in Figure 2. As can be seen, both the martensitic plateau stress and the peak stress increase linearly per Clausius-Clapeyron, with a stress rate of $d\sigma/dT = 3$ MPa/°C. The magnitude of the yield drop does not significantly change with temperatures up to -40°C, the M_d temperature of the alloy.

The flow stress corresponding to the movement of R-phase twin boundaries, S_r, decreases just slightly with increasing temperature until -40°C, at which point the stress increases so rapidly that the plateau becomes ill-defined and the measure useless.

Tests were run at -196°C at strain rates ranging from 10^{-5} sec^{-1} to 10^{-2} sec^{-1} with no statistically significant effect on the resulting tensile curves and specifically the nature of the yield drop.

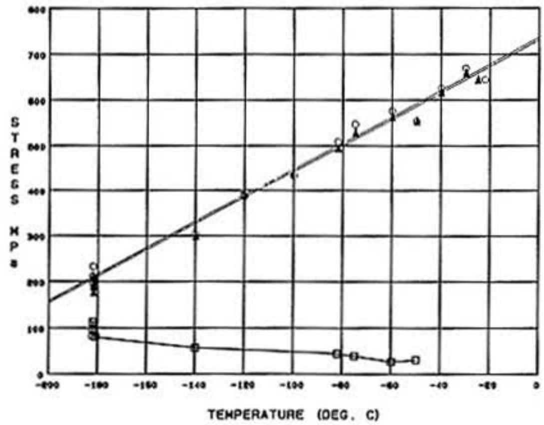


Figure 4: Temperature dependencies of S_r (■), S_m (o) and S_p (▲).

Snap Action during Deformation

The stress-strain curve shown in Figure 2 was obtained by monotonically increasing strain and allowing the stress to follow (a *strain controlled* test). Figure 5 shows the behavior of the same specimen when instead stress is monotonically increased (a *stress controlled* test). There are no differences between the two curves up until the peak stress S_m. At this point, the testing system seeks a shape that will allow an increase in stress, and must deform the specimen an additional 4% to do so. The result is that the testing machine becomes momentarily unstable and "snaps" to its new shape. The snap movement is quite audible when testing specimens of 0.250" diameter.

In a sense, this *snap action* behavior is an artifact of the speed of the testing system. One can better imagine a system of weights hanging from a wire. With weights corresponding to the stress S_m, the system is stable, but if one perturbs the system even slightly (even if only momentarily), the wire will suddenly and spontaneously extend 4% in length.

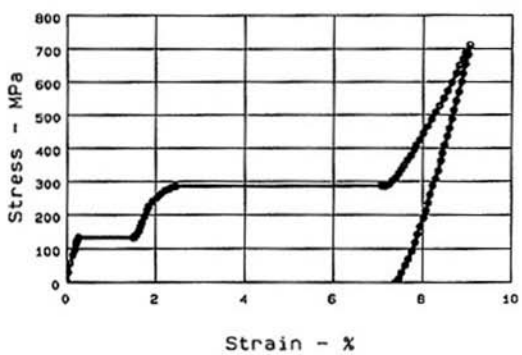


Figure 5: Stress-strain curve of NiTiFe at -196°C tested in stress control. Discrete points represent 25 points in the data acquisition system - no points were recorded between strains of 2.3% and 6.5%.

Snap Action Superelasticity

Superelasticity refers to a situation in which martensite is stress induced upon loading, then becomes unstable again during unloading, returning to the original austenitic structure and shape. In order to achieve this, deformation and unloading must occur above the A_f temperature of the alloy and below the M_d temperature. In this particular alloy, optimum superelasticity is achieved at -120°C. Figure 6 shows such behavior when loading and unloading in a strain controlled mode. The fact that the superelastic unloading does not completely restore the original shape is reflective of the fact that deformation is still below the R_s temperature of the alloy: the R-phase develops preferred variants upon loading, and is returned to those same deformed variants during reversion. For complete superelasticity, one must deform above R_s (the R-phase start temperature) and above A_f.

Note in Figure 6 that the loading yield drop is still present, and that a mirror image, diffuse inverted peak is seen during unloading (denoted "A"). There is also a peak stress at "B". These will be discussed in more detail later, but the presence of features "A" and "B" indicate that there are difficulties associated with the initiation of the martensite to austenite reversion, and with the completion of that same reaction.

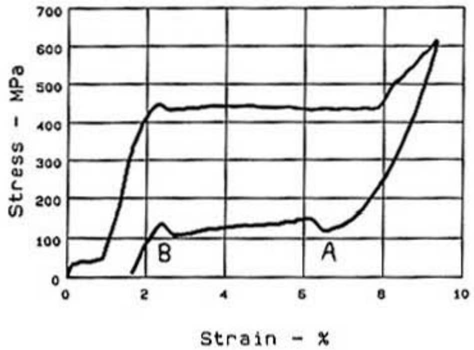


Figure 6: Tensile test performed at -120°C in strain control demonstrating superelasticity of the R-phase to martensite transformation.

It is difficult to perceive exactly what is happening at "A", a situation in which one must increase the load on a specimen in order to allow it to relax towards its original shape. The result of the instability, is a snap action upon unloading analogous to that found upon loading. When unloading in a stress control mode, an unstable and audible "snap" is observed.

Snap Action Recovery

The deformation strain imparted by the sequence shown in Figure 2 can be fully recovered by heating above the A_f temperature of the alloy. It is common, when doing so, to record the strain as a function of temperature. Figure 7 shows such a recovery profile for the sample shown in Figure 2. As should be expected from Figure 6, the bulk of the recovery takes place in a snap action recovery.

In this case the sample was deformed as shown in Figure 2, released from the testing machine and allowed to very slowly warm to room temperature with an extensometer still attached. Heating rates were varied from 0.017 °C/sec to 1.0°C/sec with no resulting effect on the shape of the curve. The recovery motion was far too rapid to record with a conventional x-y recorder. Attempts to measure the speed of recovery with a high speed data acquisition system were able to put a lower bound on the velocity of recovery of $\dot{\varepsilon} = 5000\ sec^{-1}$. This snap action shape memory effect is expected since temperature is completely analogous to stress in thermoelastic alloys.

Given the observations of Figure 7, it should be possible to set up a more common scenario: thermally cycling a tensile specimen with a fixed load applied. A shape memory alloy will alternately extend upon cooling and contract upon heating if the applied stress is above the martensitic plateau stress (S_m in Figure 2). Since the yield drop phenomenon is evident during both the forward and reverse transformations, snap action motion is detected during both heating and cooling (Figure 8). Again, both directions are independent of cooling rate, and the motion is accompanied by a very audible cracking sound. Very high stresses (over 400 MPa) are required to suppress the snap action.

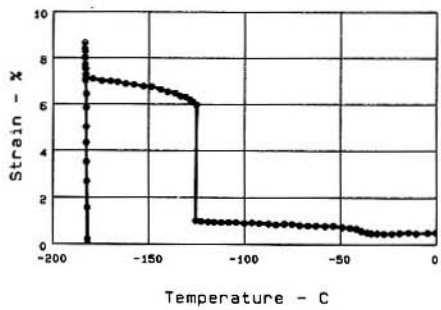
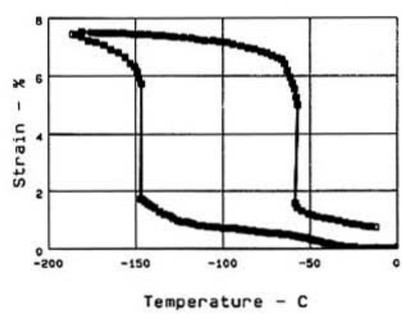


Figure 7: Recovery profile of a specimen deformed 9% at -196°C and warmed at 0.1°C/second.

Figure 8: Strain-temperature profile of a specimen cooled and then heated with a 350 MPa tensile stress applied.



The Effects of Incomplete Transformation

It is important to note that is is necessary to complete the transformation to martensite if one is to observe snap action in the reverse direction. Specifically:

1. If martensite is stress induced to completion (Figure 2), unloaded, recovered, then deformed again, the second deformation will exhibit the same yield drop and snap action characteristics.
2. In a strain controlled mode, martensite can be stress induced, but unloaded before the end of the plateau. In this case, snap action recovery is not observed since the forward transformation was incomplete.
3. If again the specimen is unloaded prior to completing the transformation to martensite, then loaded directly, no yield drop is found.
4. No strain ageing effects are observed: it makes no difference whether one waits several days, or seconds prior to reloading in the above manner.

DISCUSSION

Before discussing microscopic mechanisms for the above effects, it is worthwhile summarizing the observations that must be allowed by a successful explanation:

1. The yield drop is diffuse, without either leading or trailing serrations.
2. The phenomenon is observed in both transformational directions.
3. The behavior is only found in polygonized microstructures.
4. The yield drop and resulting snap action are, to the first order, strain rate and temperature rate insensitive.
5. An estimated 10-15% martensite is present prior to achieving the peak stress level, S_m.
6. It is necessary to complete the transformation to martensite in order to observe snap action effects during reversion.

Pinning of martensitic boundaries by deformation debris or by solute atoms cannot explain the above characteristics. Specifically, pinning would have a serrated yield. It is also inconsistent with the various incomplete cycling observations described earlier.

Explanations based upon autocatylitic nucleation are successful in explaining the incomplete cycling observations as well as the diffuse nature of the yield point. In this case one assumes that nucleation of the first plates is quite difficult, but as soon as the first plates form, they are able to trigger subsequent nucleation events and thus the transformation proceeds at a reduced stress level. Such an argument can even be applied to the reversion phenomenon. It does not, however, allow for the relatively large volume fraction of martensite that is formed prior to achieving the peak stress of Figure 2. Moreover, it is inconsistent with the fact that the effect is only observed in structures with very high defect densities, where one would least expect to find difficult nucleation and autocatylitic effects.

Martensite "Penning"

When a stress is applied to the austenitic structure, martensite will first nucleate upon the most potent sites, meaning upon defects which provide elastic stress fields that best accommodate the elastic energy of the martensite nucleus. Surface energy also plays a role, but is of secondary importance. The resolution of the applied shear stress on the defect, however is important: a defect that is very potent in one stress field may be of minor importance in another. Statistically, we can assume that the first plates to form are those most favorably aligned to the applied stress field - those experiencing the greatest resolved shear stress.

In the microstructure of the present alloy, a single nucleation event is essentially *penned* in by the low angle grain boundaries. A newly nucleated martensite plate can easily propagate the length of a subgrain, but must deviate from its ideal orientation if it is to cross a low angle cell boundary. In other words, the resolved shear stress on the plate is reduced upon crossing the boundary. At this point the stress must be increased, and another nucleation site activated. Thus work hardening is observed.

Eventually, the stress is increased sufficiently to force the penned martensite plate through the low angle boundary and into the next cell. Once past the boundary, the supercooled martensite plate grows extremely rapidly until encountering the next boundary. At this second encounter the plate is more stable than in its first encounter, having decreased its surface and strain energies per unit volume. Having already sufficient chemical free energy to pass the first boundary, the second boundary presents a lesser barrier, the third even less, etc. (It is equally likely, in fact, that subsequent encounters may even correct the course of the plate, increasing the resolved shear stress.that drives its growth.) Once freed from its original cell, or pen, the plate grows with increasing rapidity. Unlike serrated yield phenomenon connected with interstitial atoms in steel, here the breakaway is gradual, with each barrier only slightly easier to cross then the previous. Note that this allows for a diffuse yield drop: not only does some transformation occur before breakthrough, but the stress needed to continue transformation after breakaway is gradually reducing to the steady state condition.

Given the above, one can easily foresee that the effect should go in both directions, since austenite must be nucleated in a fully martensitic structure. Moreover, if one does not complete the forward transformation then it is no longer necessary to nucleate austenite. In this case one should not, and does not, observe a yield drop or snap action.

Snap action while thermally cycling with a load applied is a natural extention of the above since temperature and stress are thermodynamically equivalent in this temperature range.

The term "penning" then offers playful analogy. Consider a bull, fenced in a small pen surrounded by similar small pens. The bull will stay put until sufficiently agitated to break down the first fence. Once that is down, however, the bull can take a running start at the second, and more easily break through that. The more fences that are down, the less the agitation required to break further fences and increase its range. The result might well be like that shown in Figure 9.

One further note should be made concerning the nature of the microstructural pens present in this microstructure. Although there are a great number of low angle cell boundaries, it appears as if there are also coherent high angle cell boundaries present [1]. During the warm working operation, the austenite twins, leaving bands of relatively high angle boundaries throughout the microstructure. It appears that these are in fact preserved during the recovery and polygonization processes. These higher angle, twin related boundaries may play an important role in defining the microstructural pens.

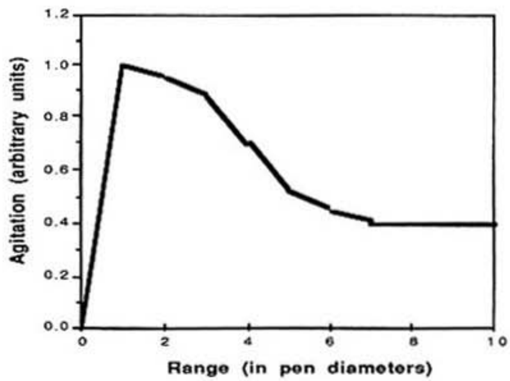


Figure 9: The diffuse yield phenomenon can be visualized by considering the range of a hypothetical bull surrounded by a series of fences and being agitated by a bull fighter.

Lüders Bands

In order to appreciate why strain energy is reduced with increasing plate size, we need to consider that the small, disconnected plates of martensite that form during the early stages of transformation must create large elastic strains in surrounding regions if a macroscopic strain is to be observed. In linking together, these martensite plates can reduce their overall strain energy.

Moreover, once these pockets are linked completely across a specimen, they form Lüders bands and can proceed quite easily. This "linking" of martensite plates to form a Lüders band plays an important role in reducing the strain energy per unit volume transformed. It is likely that the plateau stress, S_p, corresponds to the stress required to maintain motion of Lüders bands. Some evidence for this is afforded by simultaneously measuring load-displacement and load-strain. The load-displacement, curve will continuously, and without stopping, trace the curve shown in Figure 2. "Strain" however, is a localized measure. The load-strain curve will faithfully reproduce Figure 2 up until the end of the load drop, but then the recording pen will often remain stationary, waiting until the Lüders band advances to the arms of the extensometer. This provides evidence that the plateau stress, S_p, corresponds to the complete formation of Lüders bands.

ACKNOWLEDGMENTS:

The work described here was entirely done at Raychem Corporation. The authors with to acknowledge the significant contributions of Jim Proft and Weikang Yu.

REFERENCES

1. W.J. Moberly, T.W. Duerig, J.L. Proft and R. Sinclair: to be published in Acta Met.
2. H.C. Ling and R. Kaplow, Met. Trans. A, 11A, 77 (1975).
3. S. Miyazaki and K. Otsuka, Phil. Mag. A, 50, 393 (1984).
4. K. Otsuka, in Engineering Aspects of Shape Memory Alloys, edited by T.Duerig et al (Butterworth-Heinemann, London, 1990) p 36.