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LINEAR AND NON-LINEAR SUPERELASTICITY IN NiTi

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ABSTRACT

The tensile properties of the as-drawn and the annealed conditions of Ni-Ti with 50.8 at. %Ni are compared and it is shown that the former exhibits a linear superelasticity with more than 4% recoverable strain over a wide temperature range and is independent of minor nickel content variations. It is also found that the amount of elastic energy that can be stored (the area under the unloading stress-strain curve), is similar to the classical non-linear superelastic conditions. It is further shown that because of the difference in the deformation mechanisms, the as-drawn material is less prone to cyclic damage than the annealed. The mechanism for the two superelasticities are discussed, concluding that the cold working pins the martensite boundaries, preventing easy movement and preventing the thermal reversion to austenite.

INTRODUCTION

The terms "superelasticity" and "pseudoelasticity" are interchangeably used to describe the ability of shape memory alloys to undergo large deformations without the onset of plasticity. Most NiTi alloys exhibiting this property are either solution treated and aged or are cold worked and annealed below their recrystallization temperature [1,2]. In these conditions, up to 9% non-linear superelasticity can be observed due to the stress assisted martensitic transformation. Moreover, the stress during loading and unloading of such a material exhibits a plateau with little or no work hardening. This constancy of stress can in some applications [3,4] present significant advantages compared to conventional alloys [2,5].

In contrast, a linear and hysteresis-free superelasticity has been found in the cold worked conditions of martensitic NiTi [6]. Very similar effects have been observed after neutron irradiation of NiTi [7]. Although limited structural analysis has been done on this second superelasticity [6], it appears that the deformation mechanism is not transformational in nature. The purpose of this study was to further analyze the mechanical aspects of this superelasticity, and to compare these effects with conventionally transformational superelasticity in NiTi.

EXPERIMENTAL

Ni-Ti wire with 50.8 at.% Ni was drawn at room temperature to 0.5 mm diameter. Specimens for characterizing the linear superelasticity were taken directly after cold drawing. Transformational superelasticity was introduced in the wire by annealing at 500°C for two minutes in a salt bath after cold working. This heat treatment was chosen for simplicity and because it leads to exceptionally high springback strains in this particular composition. Other thermo-mechanical treatments (such as solution treating and ageing) can also introduce transformational superelasticity but were not considered in this study [1,2].

Tensile tests were conducted on both the as-drawn and the heat treated wires at temperatures ranging from -80 to 150°C. A special counter-balancing extensometer was used to measure strain in the wires, allowing free translation in the x-y plane without exerting any forces on the wire itself. Figure 1 schematically describes the parameters used to present the experimental results: σ_l (the stress plateau during loading) and σ_u (the stress plateau during unloading), are the critical stresses for causing the forward and reverse transformations, and E is the stored elastic energy (the area under the unloading curve). Some tests were also conducted on the as-drawn conditions of 50.0 and 49.4 at. % Ni wires in order to test the influence of nickel content on linear superelasticity.

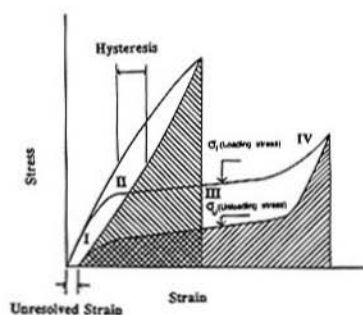


Figure 1: Schematic representation of the stress-strain curves for the as-drawn and the annealed Ni-Ti. The different stages of pseudoelasticity are numbered, I) Austenite elasticity, II) R-phase transformation, III) stress induced martensite, IV) Martensite elasticity; The stored available energy is also shaded in each curve.

RESULTS

Figure 2 compares the room temperature loading and the unloading curves of the as-drawn and the annealed specimens. The as-drawn material exhibits a low modulus "elastic" zone, and can be deformed to 4% with less than 0.3% permanent set. The slight non-linearity in loading and unloading causes a hysteresis in strain of 0.7%. Although the as-drawn loading behavior is not truly linear, the distinct plateau characteristic of transformational superelasticity is not present. The transformational material, however, shows a substantially larger non-linear recoverable strain.

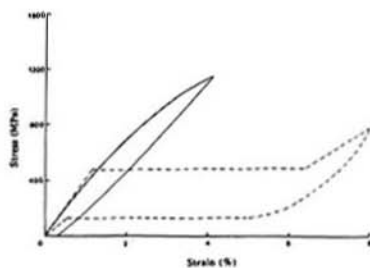


Figure 2: Stress-Strain curves at room temperature of the super-elastic and the pseudoelastic Ti-Ni50.8%at. wires pulled to 4% and 8% strain respectively and unloaded.

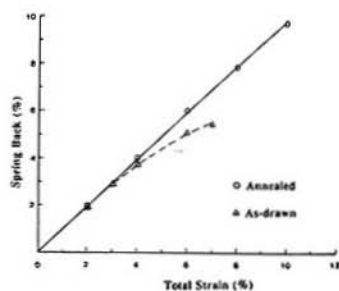


Figure 3: Recoverable strain (spring back) versus total strain at room temperature of the as-drawn and the annealed Ni-Ti wires.

The "elastic" springback can be defined by the total strain minus the permanent set. This parameter is plotted in Figure 3, showing that although transformational superelasticity provides greater springback, the as-drawn material can still elastically recover more than 5%. Several cold working reductions were tested in the case of the as-drawn superelasticity and it was found that the permanent set is not affected by the amount of cold work (Figure 4). The Youngs modulus, however, increases from ~ 30 GPa to 40 GPa and the ductility decreases from 12 to 4% by increasing the area reduction from 12 to 40%. Similarly, two other Ni contents (50.0 and 49.4 at. %) were tested. Although such variations would have very large effects on transformational superelasticity, there was virtually no effect on the as-drawn superelasticity.

One of the most serious limitations of conventional transformational superelasticity is that it is only observed over a narrow temperature range: below A_s , the material is martensitic, and shows no superelasticity; above M_d , conventional slip processes begin to interfere with the stress assisted transformation and again the permanent set is large. The as-drawn superelastic wire, however, is almost unaffected by changes in temperature. Figure 5 compares the temperature dependencies of permanent set in the two cases. The modulus of the as-drawn wire is also essentially unaffected by temperature (Figure 6).

Another difference between the as-drawn and the annealed wires is their cyclic deformation behavior. The loading stress (σ) in the superelastic material decreases and the unresolved strain increases with the number of cycles (Figure 7). This is probably due to the occurrence of small amounts of slip and the dislocation movement associated with the stress induced martensite [5,8]. This steady accumulation of plastic strain is often called ratcheting or walking. Although this stabilizes during continued cycling it creates limitations for the applications of this material. The tensile properties of the cold worked superelastic wire, however, are almost constant as long as the total strain is kept below 4%, the hysteresis decreases slightly and the recoverable strain improves (Figure 8) with the number of cycles.

Both superelastic materials are often used as "super springs" due to their high energy storage capacity (defined as $\int \sigma d\epsilon$). This energy is plotted as a function of total strain for both materials in Figure 9. It is interesting to note that the elastic energy in the as-drawn material (20% RA) after 4% strain, and in the superelastic material after 8% strain, are both nearly 20 J/cc; the greater storage capacity of the cold worked condition is due to its narrow hysteresis and higher strength levels.

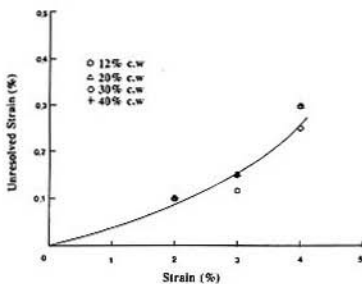


Figure 4: The amount of cold work has no influence on the unresolved strain in the as-drawn Ni-Ti wire pulled at room temperature.

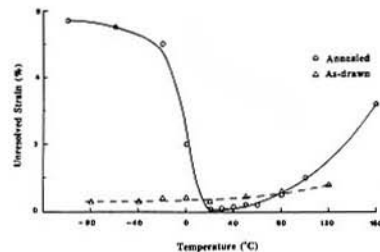


Figure 5: The unresolved strain at different temperatures of the as-drawn and the annealed Ni-Ti wires pulled to 4 and 8% strains respectively.

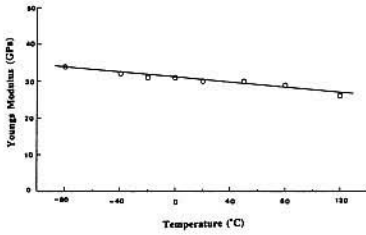


Figure 6: Young's Modulus of the as-drawn Ni-Ti wire at various temperatures. Young's Modulus=stress at 4% ϵ .

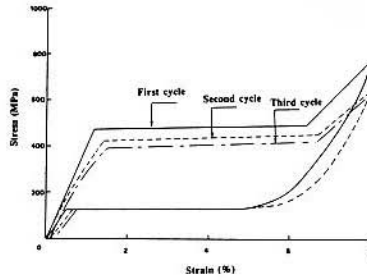


Figure 7: The influence of cycling on the stress-strain curve at room temperature of the annealed Ni-Ti wire. Only three cycles are shown for clarity. K.Otsuka et al [5] have reported similar results on this material.

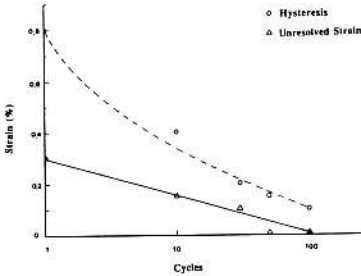


Figure 8: The variations of the hysteresis and the unresolved strain with cyclic deformation in the as-drawn Ni-Ti wire pulled to 4% strain in each cycle at room temperature and unloaded.

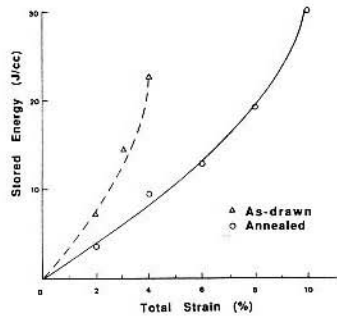


Figure 9: The stored energy per unit volume (area under the unloading stress-strain curve) of the as-drawn and the annealed Ni-Ti wires.

DISCUSSION:

The mechanism for non-linear, or transformational superelasticity in Ni-Ti, has been widely studied: martensite is stress induced and is able to undergo rather large shape changes by virtue of the fact that it can select the variant that best accommodates the imposed stress. During the shape memory process, twinned martensite is formed during cooling and is then rearranged during deformation; the martensitic stress-strain plateau is then caused by a continuing rearrangement of martensite - not by increasing the quantity of martensite. In the case of superelasticity, however, the optimum variants of martensite are formed directly from the matrix, with the volume fraction of martensite increasing along the stress-strain plateau. This progression occurs by advancement of Lüder's bands [9].

The detailed mechanism for linear superelasticity is less clear. The temperature independence shown in Figures 5 and 6 show that there is no transformation involved. In fact, we know from previous studies that the cold worked condition is fully martensitic even before a load is applied [10,11]. Thus, there are three important differences from the annealed material:

1. The cold worked martensite is apparently stable to very high temperatures. Figure 5 and 6 clearly show that the material does not revert to austenite until well over 150°C - even in Ni-rich alloys which would typically have A_s temperatures below 0°C. Residual stresses could clearly account for some increased martensite stability, but clearly not all since martensite is persisting well above M_d .
2. The martensite yield stress, or resistance to twin movement, is sharply increased by cold working. One might suppose that the martensite twin variant distribution is already in the most favorable configuration and therefore cannot further twin; but the fact that this also occurs in irradiated material indicates an interaction between the twin boundaries and the increased defect concentration must be responsible.
3. What twin movement does occur is reversed upon unloading (this is indicated by the hysteresis and non-linear nature of the effect). This type of superelasticity is termed twinning pseudoelasticity and has been reported in a variety of alloys including Au-Cd [12,13], In-Tl [14,15] and Cu-Al-Ni [16,17]. The martensite twins can be shifted from their original positions by the application of a stress, and will return to their original positions when the stress is relieved. Thus one must assume that the dislocations from the cold drawing process (or defects from the neutron irradiation) are tied up with the twin boundaries, providing a preferred low energy twin configuration. The twins can be moved during loading, but will return to this low energy configuration during unloading.

SUMMARY

A comparison of a transformational and a non-transformational martensitic superelasticity in Ni-Ti has demonstrated the following points:

1. Cold worked Ni-Ti wire exhibits a low modulus superelasticity with little hysteresis. Recoverable strains well in excess of 4% are observed over a very wide range of temperature. Although some fatigue ratcheting is observed, the effects are small when compared to Ni-Ti exhibiting transformational superelasticity. In fact, cycling improves some properties.
2. The cold worked material is capable of storing slightly greater elastic energies than the transformationally superelastic material - particularly at low strain values.
3. The mechanism by which superelasticity is achieved appears to be an interaction between defects from the cold working process and the martensite twins. These defects prevent the easy migration of twin boundaries, cause any movement that does occur to reverse itself during unloading, and stabilize the martensite to temperatures above 150°C.

Although the use of NiTi in the cold worked condition could limit the range of shapes in which the material might be used, the wide temperature range over which the superelasticity is exhibited and the superior resistance to fatigue may make them useful for many applications.

REFERENCES

1. S. Miyasaki, et al., *J. de Physique* C4(43), 255 (1982).
2. S. Miyasaki, et al., *Met. Trans* 17A, 115 (1986).
3. F. Miura et al., *Orthodontics and Dento. Orthopedics* 90(1) (1986)
4. R.M. Wood, *Acta Met.* 11, 907 (1963).
5. K. Otsuka and S. Miyazaki, SPEY 14 (Reports of Special Project Research on Energy, the Scientific Research of the Ministry of Education, Japan), 51 (1985).
6. O. Mercier and E. Torok, *J. de Physique* C4(43), 267 (1982).
7. T. Hoshiya et al., *ICOMAT-86, Jap.Inst. Met.*, 685 (1986).
8. K.N. Melton and O. Mercier, *Acta Metal.* 27, 137 (1979).
9. S.Miyazaki, et al., *Scripta Met.*, 15, 853 (1981).
10. M. Nishida, C.M. Wayman and T. Honma, *Met. Trans.* 17A, 1505 (1986).
11. G.M.Michal, *Diffusionless Transformations in TiNi*, Ph.D Thesis, Stanford University (1979).
12. D.S. Liberman, M.A. Schmerling and R.W. Karz, *Shape Memory Effects in Alloys*, J. Perkins,ed.,Plenum Press, 203 (1975).
13. A. Zangwill and R. Bruinsma, *High-Temperature Ordered Intermetallic Alloys*, Boston, Mass.26-28,Nov.pp. 529-535 (1984).
14. M. Wuttig and C. Lin, *Acta. Metall.* 31(7), 1117 (1983).
15. S. Miura, et al., "Superelastic Behavior and Aging Effect in Thermoelastic In-Tl Martensite", *Kyoto Univ.Vol.XLIII, Part 2.*,287 (1981).
16. H. Sakamoto, et al., *Scripta Met.* 15, 281 (1981).
17. A.L. Kuporev and L.G. Khandros, *Fiz. Metal. Metalloved* 32(6), 1322 (1971).