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Wide Hysteresis Shape Memory Alloys Based on the NiTiNb System

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WIDE HYSTERESIS SHAPE MEMORY ALLOYS BASED ON THE NI-TI-Nb SYSTEM

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INTRODUCTION

The first major commercial application of shape memory alloys (SMA's) was to couple aircraft hydraulic tubing[1]. A Ni-Ti based alloy was used, and the couplings were expanded and stored in liquid nitrogen. This was necessary to ensure that the coupling, once installed, remained in the austenitic phase throughout service, even down to the lowest operating temperature of -55°C.

By utilising the martensitic instability of Cu-based SMA's, a method of expanding their hysteresis was developed [2], which allowed deformed parts to be stored at ambient temperatures and installed by heating. This process was not applicable to Ni-Ti-based alloys, which although offering higher recovery forces and strains, do not show a similar

In this paper, the effect of Nb additions to Ni-Ti are reported, and it is shown that very wide hysteresis alloys can be produced. The wide hysteresis and its possible application have already been described[3], the present work discusses for the first time the metallurgy of the system..

EXPERIMENTAL

Alloys were melted by electron beam. The resulting ingots were swaged and rolled at 850°C to strip, samples cut, descaled and vacuum annealed for 30 minus at 850°C. Transformation temperatures were measured by heating the specimen to around 150°C to ensure it is fully austenitic and then cooling and subsequently re-heating under a constant load while monitoring its length change. A plot of length vs. temperature gives the hysteresis, shown schematically in Fig. 1, together with the determinations of M_S , M_f , A_S , and Af. M50 and A50 can be defined as the temperatures at which 50% of the strain change has occurred on cooling and on heating respectively, the difference A50-M50 providing a convenient measure of hysteresis width.

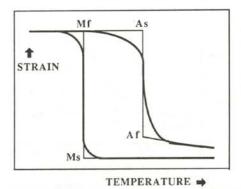


Fig. 1 Transformation temperature measurement by thermal cycling under constant load

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RESULTS

Fig. 2 shows the M_{50} and A_{50} temperatures of a 44Ti 47Ni 9Nb alloy (all compositions are in at. %) as a function of stress. A linear dependence is found, and extrapolating to zero load it can be seen that A_{50} - M_{50} is 60°C. Also shown on the graph are data for a 50 at. % Ni binary alloy, with a zero load A_{50} - M_{50} of 35°C, a significantly narrower hysteresis than for the Ni-Ti-Nb alloy.

Examination of Fig. 2 also shows that the hysteresis width of both alloys increases with increasing load, but the increase is much greater for the Nb containing alloy. At 285 MPa the value of A_{50} - M_{50} has increased to 116°C.

It was suggested [4] that there is a dependence of the hysteresis width on the yield stress at $M_{\rm S}$, since both can be related to a friction stress to move the austenite/martensite interface. Fig. 3 shows data plotted for a range of Ni-Ti based alloys, including -Fe, -V, -Cu and -Nb ternaries. The general trend is apparent but a large scatter is obtained. It can be seen that the 44 Ti 47 Ni 9 Nb alloy is at the top end of the hysteresis range and falls outside the scatter band of data points. This might imply a different mechanism controlling the hysteresis. However in view of the variation shown this may not be significant.

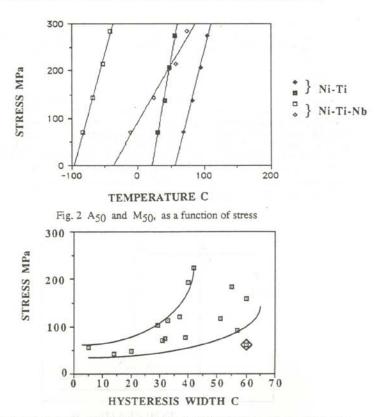


Fig. 3 Hysteresis Width vs. Yield Strength at M_S for Ni-Ti based alloys. The data point outside the scatter band is 44 Ti 47N 9Nb.

One of the features of this mechanical method of measuring transformation temperatures, is that the amount of strain occurring during cooling through the transformation also increases with stress. A series of specimens were therefore isothermally deformed in the martensitic phase to different total strains, and the recovery temperatures (A_s) measured. The results for the 44 Ti 47 Ni 9 Nb alloy, Fig. 4 shows that As increases with deformation strain, however at larger strains the curve flattens, i.e., the maximum achievable recovery temperature saturates at around 16% total strain. It is interesting to note from Fig. 4 that the deformation strains needed to maximize A_s are higher than those normally used in Ni-Ti alloys. Nevertheless, the recovery strains remain usefully high, Fig. 5.

A specimen was deformed to 3% total strain above M_d , i.e., in the fully austenitic condition, and the hysteresis width subsequently measured. No increase was found compared with an underformed sample. This demonstrates that the plastic deformation needed to widen the hysteresis must occur in the martensitic phase.

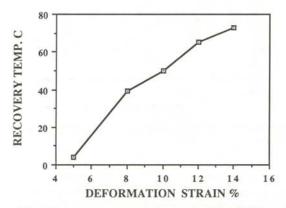


Fig. 4 Recovery temperature As as a function of deformation strain

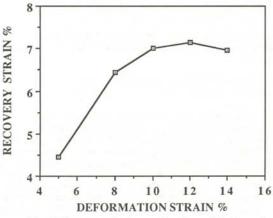


Fig. 5 Recovery Strain as a function of Deformation Strain

The process which utilizes the martensitic instability of copper based SMA's results in the hysteresis being expanded for the first heating cycle only [2]. It is therefore interesting to compare first and second cycle $A_{\rm S}$ of this Ni-Ti-Nb alloy after a large initial deformation in the martensite. Fig. 6 . After the initial deformation, all subsequent testing was done with no applied load. However on cooling back into the martensitic phase, the internal stress resulting from the original 13% deformation not being fully heat recovered, leads to a two-way effect [5]. As can be seen from Fig. 6, the second (and in fact all subsequent cycles) $A_{\rm S}$ value is significantly lower than that measured during the first cycle. The effect of the over-deformation is thus to increase $A_{\rm S}$ for the first heating cycle, after which it reverts to its original value. $M_{\rm S}$ and $M_{\rm f}$ are unaffected by the over-deformation.

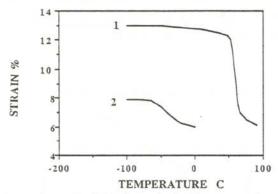


Fig. 6 Strain of a specimen after deforming and unloading, measured on the first and second heating cycles

Optical metallography of the as-cast 44 Ti 47 Ni 9 Nb alloy revealed (Fig. 7a) that the microstructure consists of primary dendrites of the β -phase surrounded by a eutectic-like structure containing particles of a Nb-rich phase shown by EDAX to be essentially pure Nb with small amounts of Ni and Ti in solution. After hot working, the banded structure shown in Fig. 7b is produced, indicating that all phases present are ductile.

DISCUSSION

It is clear that overdeformation widens the hysteresis of Ni-Ti alloys, and that the effect is particularly pronounced in Nb containing materials. From a mechanistic point of view, two questions then arise:

- 1) what is responsible for the widening in binary Ni-Ti and
- 2) what is special about Nb alloys?.

One distinctive microstructural feature of Ni-Ti-Nb is the presence of deformable Nb particles. It therefore seems logical that it is their presence which gives these alloys the readily expandable hysteresis. As the composite structure of martensite and Nb particles is strained, the martensite deforms with a significant reversible twinning component, while the Nb particles deform plastically. In order for the martensite to reversibly transform back to austenite, any lattice rotation associated with the deformation of the particles also has to be reversed. It is proposed that the energy required to restore these particles towards their original shape as the martensite tries to revert results in a supersaturation effect and leads to higher $A_{\rm S}$ temperatures. Clearly the greater the total strain, the more strain is partitioned to the Nb particles and the higher is the resulting $A_{\rm S}$.

With respect to the widening of the hysteresis in binary (or non-particle containing) alloys, the situation is less clear. A possible explanation is that plastic deformation in the martensite results in dislocations which jog the coherent twin planes and result in a friction force which has to be overcome on reversion. In both of these cases, if the deformation is done in the austenite, then the dislocations have only an elastic effect and the martensite plates nucleate around them, possibly incorporating them into the incoherent interfaces and leading to a negligable friction effect. The dislocations introduced in the austenitic phase will thus, with their local strain field, help select those variants of martensite which nucleate but not significantly influence the hysteresis width.

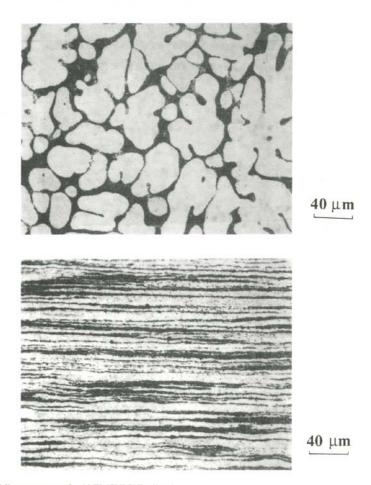


Fig. 7 Microstructure of a 44 Ti 47Ni 9Nb alloy in

a) the as-cast condition and

b) after hot working at 850°C

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CONCLUSION

It has been shown that Ni-Ti Nb alloys can have a very wide transformation hysteresis, and that this is associated with the presence of soft deformable particles of niobium. These new alloys have great potential as mechanical components to join, fasten

REFERENCES

- J. D. Harrison and D. E. Hodgson in Shape Memory Effects in Alloys, edited by J. Perkins (Planum Press Publishers, New York p. 517, (1975).
 G. B. Brook, P. L. Brooks and R. F. Iles

 U.S. Patent Numbers 4,036,669; 4,067,752; 4,095,999.

 K. N. Melton, J. Simpson and T. W. Duerig, Proc. Int'l Conference on Martensitic Transformations ICOMAT-86, (Japan Institute of Metals)
- p 1053 (1986). K. N. Melton and O. Mercier Acta Met 29, 393-398 (1981).
- 5. J. Perkins Scripta Met 8, 1469 (1974).