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Wide Hysteresis NiTiNb Alloys

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Introduction

In order to maintain the integrity of a shape memory coupling or fastener, it is essential that the installed parts remain austenitic throughout their service life. If they become martensitic, the recovery stresses will be reduced to the martensitic yield stress, or even worse, the two-way effect will cause the joint to physically separate. In the past, this has mandated the use of cryogenic alloys which remain austenitic at all normal service temperature, but must be expanded, stored, inventoried and assembled in liquid nitrogen to prevent premature recovery.

All solutions to this problem involve increasing the hysteresis of the alloys, or more precisely, separating A_s from M_s as far as possible, the reasoning being that M_s controls the stress decay process mentioned above, while A_s dictates the maximum storage temperature. Shipping temperatures can reach 45°C in extreme cases, so the unstressed A_s of a successful wide hysteresis alloy must be at least that. How low the zero stress M_s (M_s^*) must be, however, is rather complex since fasteners and couplings are under stress and M_s is a strong function of applied stress. In general one can calculate this from the following equation:

$$M_s^* < T_0 - \sigma_r (d\sigma/dT)^{-1} \qquad \text{Equ. 1}$$

where T_0 is the lowest expected service temperature, $d\sigma/dT$ is the stress rate of the alloy (typically 5 MPa/°C for NiTi), and σ_r is the minimum recovery stress needed to maintain product integrity. For most applications M_s^* must be below -90°C.

Although there are disordered shape memory alloys which show large hysteresis behaviors (β-Ti (1)) and iron based alloys (2), for example) long range order continues to be an important criteria for substantial shape memory strains and recovery stresses. A_s is essentially the same as M_s in CuZnAl and exceeds M_s by only 20°C in NiTi. In order to provide what has been dubbed "heat-to-shrink" capabilities the hysteresis behaviors must be significantly expanded. Methods to expand the hysteresis of Cu-Zn-Al based alloys have been known for some time (3), but unfortunately this system has several attributes that make it imperfectly suited for coupling and fastener applications (poor

resistance to stress corrosion cracking, rapid stress relaxation at temperatures as low as 100°C, and recovery strains of only 3-5%). Although the Ni-Ti alloy system inherently offers better mechanical properties, until recently it has not been possible to achieve the desired hysteresis characteristics. The first reports of such success were, in fact, reported only 3 years ago (4-6) in a NiTi alloy containing some 9 at.% Nb. Since that time, several products have been brought into production using this important characteristic.

This paper reviews the microstructure and properties of these NiTiNb alloys and proposes a mechanism for the observed large hysteresis effects. The alloy itself is a 47.0 at.% Ni-44.0 at.% Ti-9.0 at.% Nb composition, was melted in vacuum, hot rolled and annealed at 850°C in vacuum prior to all tests.

Microstructural

The microstructures of the NiTiNb alloys are remarkably different from binary NiTi alloys and other ternary compositions (7). In the as-cast condition (Figure 1), one observes a large volume fraction of second phase, forming as a eutectoid with NiTi. Hot working breaks down the eutectoid structure, but the large volume fraction of second phase persists (Figure 2), taking on a globular or elliptical morphology. The matrix phase has been shown (8) to be essentially pure NiTi, taking into solution only a small amount of Nb. The second phase, on the other hand, has been identified to be nearly pure body centered cubic Nb; if one compares the lattice parameter of the Nb phase with that of pure Nb, one concludes that the phase may in fact be pure (3.296Å for the second phase versus 3.290Å for pure niobium). Thus the microstructure is of a bimodal nature: a matrix of ordered intermetallic NiTi with the B2 structure, and a dispersion of nearly pure BCC niobium, which one would suppose to be very soft compared to the austenitic phase of the NiTi.
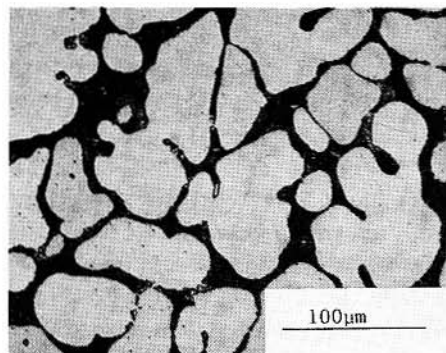

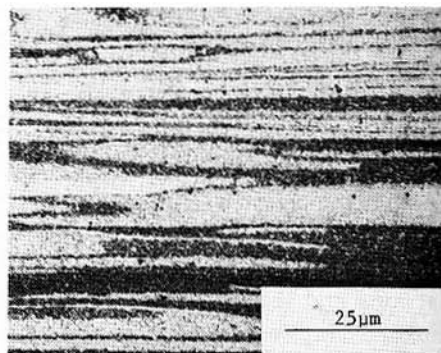Fig. 1: As-cast NiTiNb structure showing the light NiTi phase and dark eutectoid.

Fig. 2: Hot rolled NiTiNb with bands of the eutectoid Nb-NiTi mixture.

Deformation Behavior

During deformation the phase mixture remains thermoelastic and exhibits shape memory. Deformation below M_s is characterized by the variant reorientation plateau typical of NiTi binary alloys, with the exception that the plateau stress (stress needed to move twin boundaries) is somewhat greater: 250 MPa versus 150 MPa. The length of the plateau and the irreversible yield point appear to be largely unaffected by the dispersion. During heating, the deformed martensite will revert and recover its original shape (Figure 3). The recoverable strain in these alloys is as great as one would expect in binary alloys, however it is interesting to note that recovery is imperfect even after small deformations. Binary alloys may recover perfectly after deformations of over 7%.
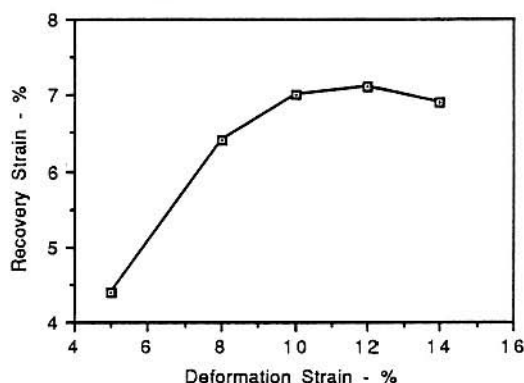

Fig. 3: Shape recovery strain (in tension) as a function of otal deformation strain.
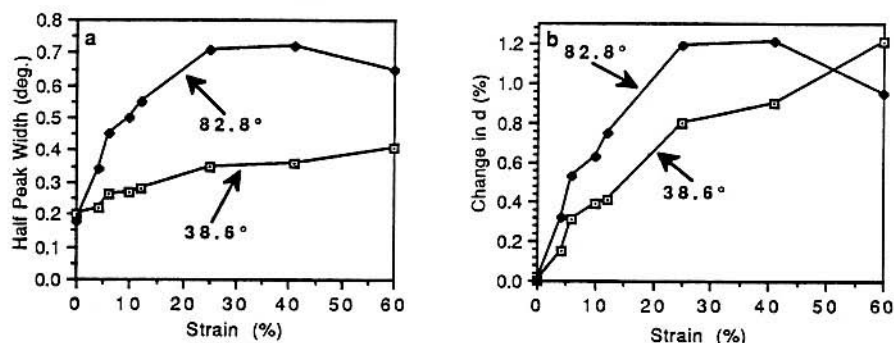

Fig 4: The relationship of macroscopic tensile deformation width X-ray peak width and change in lattice strain in the niobium phase.

The deformation behavior of the niobium phase is more difficult to study. As said earlier, the yield stress of annealed niobium is very low (on the order of 200 MPa). Based on the heat treatment sequence described earlier, one would expect the niobium second phase to deform well before the matrix begins to slip, and in fact, to have roughly the same flow stress as the twinning reorientation plateau of the matrix. In order to demonstrate this, tensile specimens were deformed to various strains and then subjected to a particle extraction process (5). The extracted particles were then examined via X-ray diffraction to look for line broadening (indicative of plastic deformation). This method quite clearly demonstrated that the particles in fact deform after deformations as small as 4% (Figure 4). The importance of this is that the total deformation strain is apparently partitioned into irreversible and reversible parts, the irreversible component being accommodated by the second phase. Further, from Figure 3 we can see that the irreversible deformation does not prevent shape recovery from occurring.
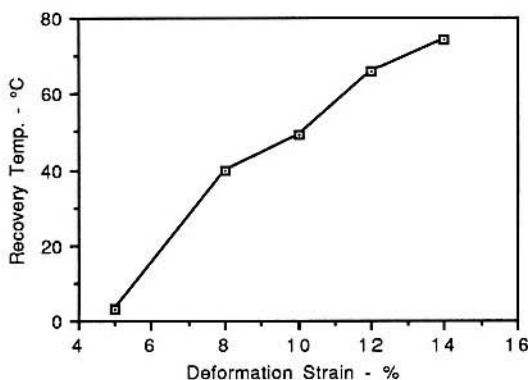
Fig. 5: The effect of deformation strain on A_s'.

Thermal hysteresis
The hysteresis of NiTiNb (as measured by electrical resistivity) was found to be somewhat greater than that of a binary NiTi alloy. Specifically, M_s, M_f, A_s and A_f were found to be -90, -175, -85, and -35°C. If one defines the hysteresis as:

$$(M_s+M_f)/2 - (A_s+A_f)/2 \qquad \text{Equ. 2}$$

one finds a hysteresis of 72.5°C - nearly twice that of binary NiTi. What is more important, however, is the thermal hysteresis after deformation. The effect of deformation upon A_s can easily be measured by deforming in tension below M_s

and then monitoring strain while heating without load. The results of such an experiment are shown in Figure 5, and clearly demonstrate that A_s is rather dramatically increased by relatively small strains. This displaced A_s has been termed A_s'. It should be pointed out that similar effects have been observed in binary NiTi alloys, but the effects are much smaller in magnitude(4). Measuring the effects of deformation upon M_s without an applied stress is somewhat more difficult, but can still be done by monitoring the two-way effect during subsequent cooling. These experiments show that M_s is not affected by the tensile deformation. Thus deformation is shown to increase hysteresis.

Finally, we can look at the second cycle A_s, meaning A_s after first heating above A_s' to recover the original shape, then cooling below M_s and then measuring A_s during the next heating cycle. This second cycle A_s is restored to the original, undeformed value. Thus the increase in A_s to A_s' is temporary, affecting only the first heating. From Figure 5 it is evident that one can achieve A_s' values in excess of 50°C, which provides a useful and stable storage condition.

Mechanism of hysteresis expansion
Relatively little is understood about what controls the hysteresis of NiTi-based alloys. Copper additions are well known to reduce hysteresis (10), but the exact mechanism of the effect is not understood. Alloys transforming to the R-phase prior to martensite formation and then transforming directly back to austenite upon heating exhibit slightly larger hysteresis loops then do materials not exhibiting R-phase behavior. This is easily understood on the basis of driving energy: the formation of R-phase from austenite reduces the driving force for martensite formation and thus suppresses M_s. Although there is some evidence that very long ageing times can slightly increase the hysteresis of Ni-rich alloys, generally speaking processing effects do not affect hysteresis. In this regard, the NiTiNb system would seem to be an exception. The second unique aspect of NiTiNb is that thermal hysteresis can be dramatically increased by relatively small deformations - deformations that do not, apparently, interfere with the memory effect.

The second of these features can be explained by considering the deformation characteristics of the model microstructure shown in Figure 6. Figure 6a shows the undeformed microstructure: a twinned martensite matrix with islands of soft second phase. Since we have already demonstrated that both phases deform, the deformed microstructure should look like that of Figure 6b: the martensite is detwinned (showing a biased variant population) and the particles have been irreversibly deformed. Thus the total deformation is divided
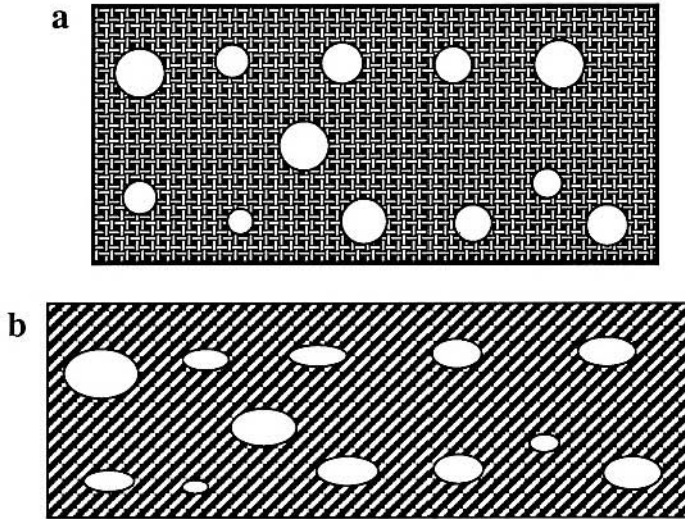
Figure 6: A schematic representation of how the NiTi-Nb phase mixture deforms: in (a), the undeformed structure is represented by spherical Nb particles in a randomly twinned martensitic NiTi matrix; after deformation (b), the particles are deformed and the martensitic twins develop a preferred variant. In order for the matrix to recover, the particles too must be deformed back to their original shape (a), thus there is a stress resisting recovery and hysteresis is expanded.

into reversible and irreversible parts. During heating, the matrix tries to recover its original shape, but in doing so it must redeform the islands - thus the islands resist the shape recovery process effectively providing an frictional stress. Since the recovery stress of the matrix is substantially greater than the flow stress of the niobium particles, the shape memory process will take place despite the biasing stress from the islands, but A_s should be increased by the frictional stress, and the magnitude of the shift should be governed by the Clausius-Clapeyron behavior:

$$\Delta A_s = \sigma_f^{Nb} \ (d\sigma/dT)^{-1} \qquad \text{Equ. 3}$$

Where σ_f^{Nb} is the flow stress of the niobium particles. In fact if one assumes 200 MPa for σ_f^{Nb} and 5 MPa/°C for $d\sigma/dT$ one expects an increase in A_s of 40°C: very near observed shifts. Once redeformed, the particles should again have no

influence on transformation temperature, so M_s and the second cycle A_s are restored to their original values. It is interesting to note the delicate balance involved in this process: if the islands are too strong, they will not deform nor play any significant role in the process, and if they are too soft they will not have a significant stress biasing effect.

Several other macroscopic features of the the overall process are expected and are in fact observed:

1. Larger deformations lead to a greater partitioning of irreversible strain and thus lead to greater A_s' values.

2. Deforming above M_s will increase the plateau stress and again partition more strain to the irreversible component; again A_s' is increased.

3. The work output is reduced since a certain amount of work must be expended redeforming the particles, but the recovery stress in a rigidly constrained situation is not significantly reduced by the presence of the particles since no redeformation is required.

The reasons for the expansion of the undeformed hysteresis are less clear but might be explained by a similar idea. Here, one can imagine that the martensite is stabilized in the vicinity of the second phase particles due to participation in the accommodation process. That is, martensite plates that progress towards the particles cause small local deformations in the particles, which somewhat alleviate the difficulties in martensite accommodation. The clear proof of this would be if the martensite surrounding the particles were to be free of internal twins. There has not yet been confirmation of this, but early studies do indicate differences in the internal martensite structure in the vicinity of the niobium particles.

References

(1) C. Baker: Met. Sci. J. 5 (1971) 92.

(2) A. Nagasawa: J.Phys. Soc. Jap. 30 (1971) 1505.

(3) G.B. Brook, P.L. Brooks and R.F. Iles: U.S. Patent 4,036,669 (1977).

(4) L.C. Zhao, et al.: Transformation and Mechanical Behavior of a NiTiNb Shape Memory Alloy., Proceedings of the 1988 Meeting of the MRS in Tokyo.

(5) L.C. Zhao, et al.: The Study of Niobium Rich Precipitates in a Ni-Ti-Nb Shape Memory Alloy., submitted to Scripta. Met.

(6) K.N. Melton, J.A. Simpson and T.W. Duerig: ICOMAT-86, (1986) 1053.

(7) J.A. Simpson and D. Stoeckel: Pract. Met. 23 (1986) 357.

(8) J.A. Simpson, K.N. Melton and T.W. Duerig: U.S. Patent 4,131,094 (1986).

(9) J.A. Simpson, K.N. Melton and T.W. Duerig: U.S. Patent 4,770,725 (1988).

(10) O. Mercier and K.N. Melton: Met. Trans. 10A (1979) 387.