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TiNi Shape Memory Alloys

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Ti-Ni Shape Memory Alloys

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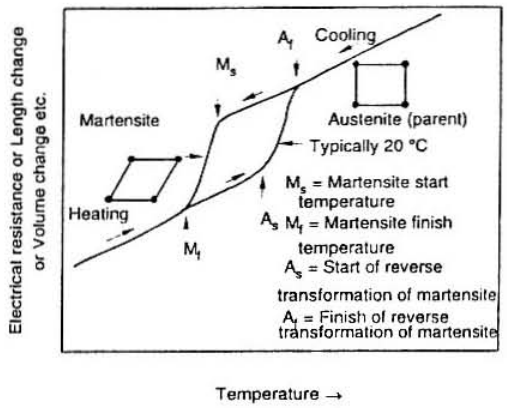
This datasheet describes some of the key properties of equiatomic and near-equiatomic titanium-nickel alloys with compositions yielding shape memory and superelastic properties. Shape memory and superelasticity *per se* will not be reviewed; readers are referred to Ref 1 to 3 for basic information on these subjects. These alloys are commonly referred to as nickel-titanium, titanium-nickel, Tee-nee, Memorite™, Nitinol, Tinel™, and Flexon™. These terms do not refer to single alloys or alloy compositions, but to a family of alloys with properties that greatly depend on exact compositional make-up, processing history, and small ternary additions. Each manufacturer has its own series of alloy designations and specifications within the "Ti-Ni" range.

A second complication that readers must acknowledge is that all properties change significantly at the transformation temperatures M_s, M_f, A_s, and A_f (see figure on the right and the section "Tensile Properties"). Moreover, these temperatures depend on applied stress. Thus, any given property depends on temperature, stress, and history.

Effect of phase transformation



Schematic illustration of the effects on a phase transformation on the physical properties of Ti-Ni. All physical properties exhibit a discontinuity, characterized by the transformation temperatures shown.
Source: C.M. Wayman and T.W. Duerig, *Engineering Aspects of Shape Memory Alloys*, T.W. Duerig, *et al.*, Ed., Butterworth-Heinemann, 1990, p 10

Product Forms and Applications

Titanium-nickel is most commonly used in the form of cold drawn wire (down to 0.02 mm) or as barstock. Other commercially available forms not yet sold as standard product would include tubing (down to 0.3 mm OD), strip (down to 0.04 mm in thickness), and sheet (widths to 500 mm and thicknesses down to 0.5 mm). Castings (Ref 4), forgings and powder metallurgy (Ref 5) products have not yet been brought from the research laboratory.

Typical Conditions. Titanium-nickel is most commonly used in a cold worked and partially annealed condition. This partial anneal does not recrystallize the material, but does bring about the onset of recovery processes. The extent of the post-cold worked recovery depends on many aspects of the application, such as the desired stiffness, fatigue life, ductility, recovery stress, etc. Fully annealed conditions are used almost exclusively when a maximum M_s is needed. Although the cold worked condition does not transform and does not exhibit shape memory, it is highly elastic and has been considered for many applications (Ref 6).

Response to Heat Treatment. Recovery processes begin at temperatures as low as 275 °C (525 °F). Recrystallization begins between 500 and 800 °C (930 and 1470 °F), depending on alloy composition and the degree of cold work.

Aging of unstable (nickel-rich) compositions begins at 250 °C (525 °F), causing the precipitation of a complex sequence of nickel-rich precipitates (Ref 7), as these products leach nickel from the matrix, their general effect is to increase the M_s temperature. The solvus temperature is about 550 °C (1020 °F).

Applications for titanium-nickel alloys can be conveniently divided into four categories (Ref 8):

- *Free recovery (motion)* applications are those in which a shape memory component is allowed to freely recover its original shape during heating, thus generating a recovery strain (Ref 9).
- *Constrained recovery (force)* applications are those in which the recovery is prevented, constraining the material in its martensitic, or cold, form while recovering (Ref 9). Although no strain is recovered, large recovery stresses are developed. These applications include fasteners and pipe couplings and are the oldest and most widespread type of practical use.
- *Actuators (work)* applications are those in which there is both a recovered strain and stress during heating, such as in the case of a titanium-nickel spring being warmed to lift a ball (Ref 10). In these cases, work is being done. Such applications are often further categorized according to their actuation mode, e.g., electrical or thermal.
- *Superelasticity (energy storage)* refers to the highly exaggerated elasticity, or springback, observed in many Ti-Ni alloys deformed above A_s and below M_d (Ref 11). The function of the material in such cases is to store mechanical energy. Although limited to a rather small temperature range, these alloys can deliver over 15 times the elastic motion of a spring steel.

Special Properties

Many shape memory-related properties are discussed in subsequent sections (transformation temperatures, superelasticity, etc.). Some properties, however, are strictly peculiar to shape memory alloys and cannot be conveniently categorized in standard outline forms. The more important of these properties are discussed below.

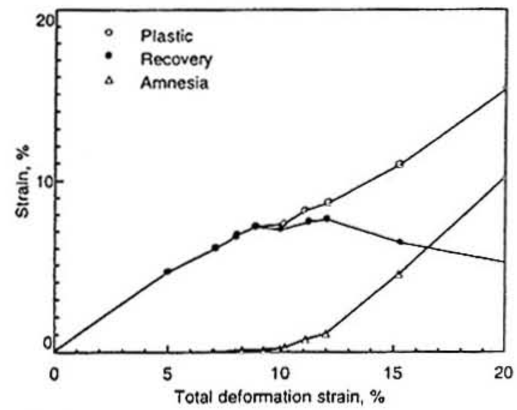
Free-recoverable strain in polycrystalline titanium-nickel can reach 8%, but is limited to a maximum of 6% if complete recovery is expected.

Applied stresses opposing recovery reduce recoverable strain. Clearly, stronger alloys will be affected less by opposing stresses. Work output is maximized at intermediate stresses and strains.

Recoverable stresses generally reach 80 to 90% of yield stress. In fact, alloy behavior depends on numerous factors, including the compliance of the resisting force and the constraining strain (Ref 9 and 12). Typical values are as follows:

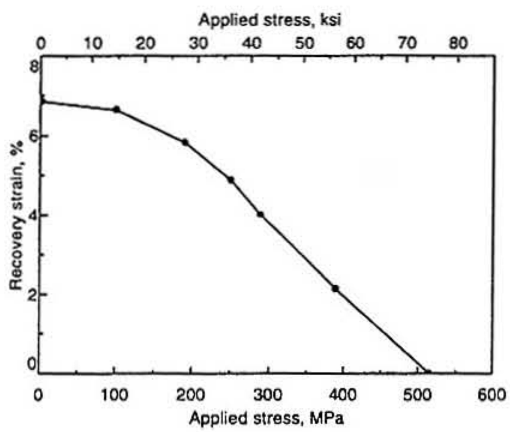
Condition	Recovery stress, MPa
Annealed barstock	400
Cold worked barstock annealed at 500 °C (930 °F)	700
Cold worked wire annealed at 400 °C (750 °F)	1000

Free recovery behavior



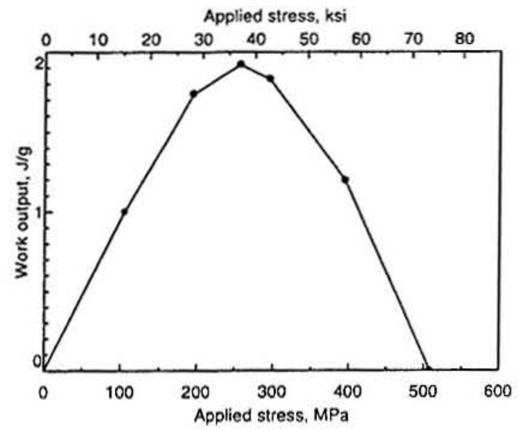
Ti-Ni-Fe barstock with 50 at.% Ni and 3% Fe fully annealed, tested in uniaxial tension. After deforming Ti-Ni to various total strains (x-axis), the material springs back to the plastic strain levels shown by the open circles. After heating above A_f, most of the strain is recovered, but some amnesia persists. The difference between the plastic strain and the amnesia is the recoverable strain (closed circles). Source: J.L. Proft and T.W. Duerig, *Engineering Aspects of Shape Memory Alloys*, T.W. Duerig *et al.*, Ed., Butterworth-Heinemann, London, 1990, p 115

Effects of opposing stresses on recovery strain



Ti-Ni-Fe barstock with 50 at.% Ni and 3% Fe fully annealed, tested in uniaxial tension.
Source: J.L. Proft and T.W. Duerig, *Engineering Aspects of Shape Memory Alloys*, T.W. Duerig *et al.*, Ed., Butterworth-Heinemann, London, 1990, p 115

Work output of a Ti-Ni alloy



Ti-Ni-Fe barstock with 50 at.% Ni and 3% Fe in a work-hardened condition, tested in uniaxial tension.
Source: J.L. Proft and T.W. Duerig, *Engineering Aspects of Shape Memory Alloys*, T.W. Duerig *et al.*, Ed., Butterworth-Heinemann, London, 1990, p 115

Chemistry and Density

Density, 6.45 to 6.5 g/cm^3

Titanium-nickel is extremely sensitive to the precise titanium/nickel ratio (see figure below). Generally, alloys with 49.0 to 50.7 at.% titanium are commercially common, with superelastic alloys in the range of 49.0 to 49.4 at.% and shape memory alloys in the range of 49.7 to 50.7 at.%. Binary alloys with less than 49.4 at.% titanium are generally unstable. Ductility drops rapidly as nickel is increased.

Binary alloys are commonly available with M_s

temperatures between –50° and +100 °C (–58 to 212 °F). Commercially available ternary alloys are available with M_s temperatures down to –200 °C (–330 °F). Titanium-nickel is also quite sensitive to alloying additions.

Oxygen forms a $Ti_4Ni_2O_x$ inclusion (Ref 13), tending to deplete the matrix in titanium, lower M_s, retard grain growth, and increase strength. Levels usually are controlled to <500 ppm. Nitrogen forms the same compound and has an additive effect to oxygen.

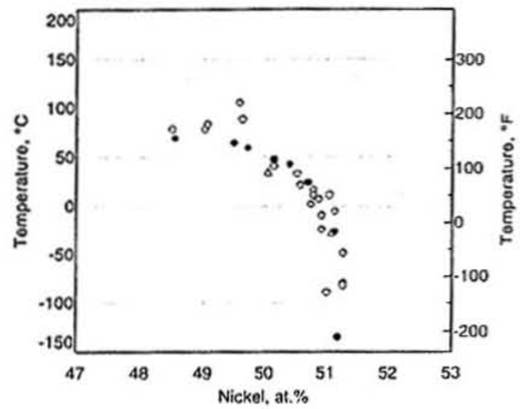
Fe, Al, Cr, Co, and V tend to substitute for nickel, but sharply depress M_s (Ref 14 to 16), with V and Co being the weakest suppressants and Cr the strongest. These elements are added to suppress M_s while maintaining stability and ductility. Their practical effect is to stiffen a superelastic alloy, to create a cryogenic shape memory alloy, or to increase the separation of the R-phase from martensite.

Pt and Pd tend to decrease M_s in small quantities (~5 to 10%), then tend to increase M_s, eventually achieving temperatures as high as 350 °C (660 °F) (Ref 17).

Zr and Hf occasionally have been reported to increase M_s, but are generally neutral when substituted for titanium on an atomic basis.

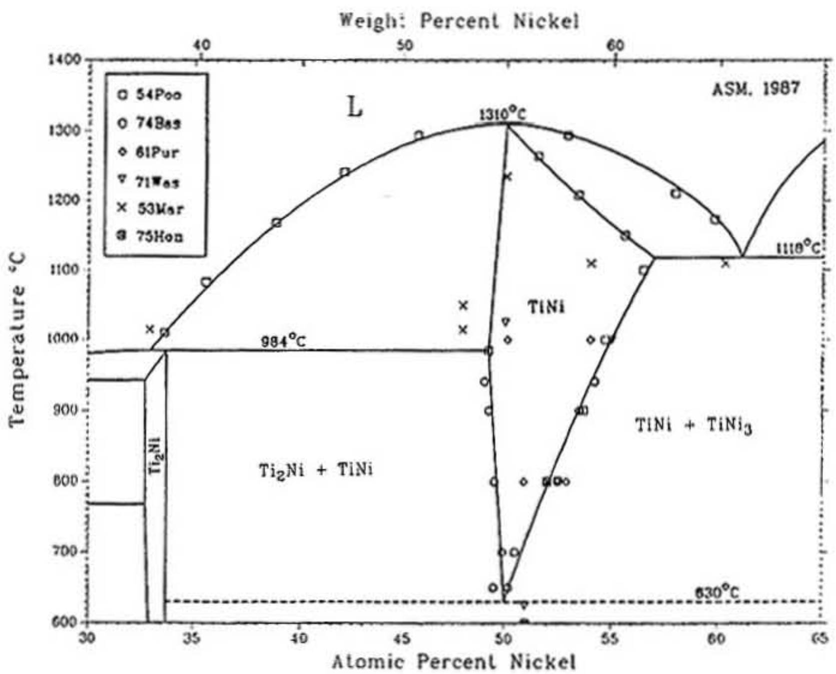
Nb and Cu are used to control hysteresis and martensitic strength. Nb is added to increase hysteresis (desirable for coupling and fastener applications), and copper (Ref 19) is added to reduce hysteresis (for actuator applications).

Effect of composition on M_s



M_s temperatures in nickel-titanium alloys are extremely sensitive to compositional variation, particularly at higher nickel contents. Source: K.N. Melton, *Engineering Aspects of Shape Memory Alloys*, T.W. Duerig *et al.*, Ed., Butterworth-Heinemann, 1990, p 10

Central Portion of Ti-Ni Phase Diagram

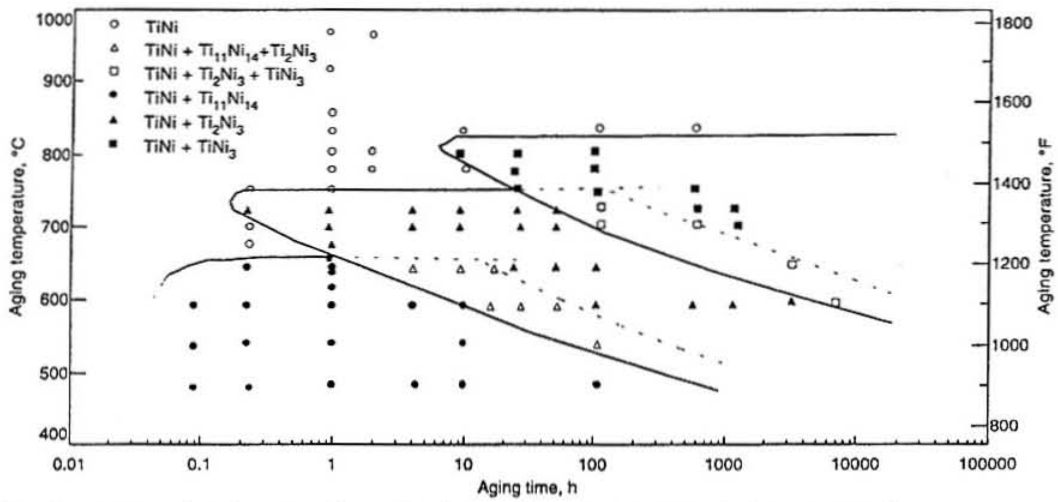


Phases and Structures

Crystal Structure

The high-temperature austenitic phase (β) has a B2, or CsCl ordered structure with a_o = 3.015 Å. The most common martensitic structure (*B*19′) has a complex monoclinic structure with a = 2.889 Å, b = 4.120 Å, c = 4.622 Å, and β = 96.8° (Ref 20). The M_s can range from <–200 to +100 °C (–328 to 212 °F). It is worth noting that there is also a "transition" structure that preceded the martensite, called the R-phase with a rhombohedral structure (Ref 21). Although this R phase exhibits a number of interesting properties, it will not be reviewed extensively here.

Time-temperature-transformation curve



Time-temperature-transformation curve for Ti-51Ni, which shows precipitation reactions as a function of temperature and time.
Source: M. Nishida, C.M. Wayman, and T. Honma, *Metall. Trans. A*, Vol 17, 1986, p 1505

Transformation Products

The T-T-T diagram shows the aging reactions in unstable (>50.6% Ni) titanium-nickel alloys (Ref 7). In general, $TiNi \rightarrow Ti_{11}Ni_{14} \rightarrow Ti_2Ni_3 \rightarrow TiNi_3$ as the aging temperature increases or as time increases at a constant temperature. These precipitation reactions can be readily monitored via transformation temperature or mechanical-property measurements.

Physical Properties

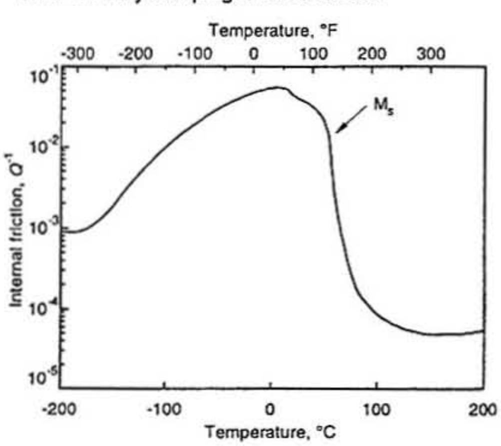
Damping Characteristics

Internal friction and damping of titanium-nickel alloys are dramatically affected by temperature changes (see figure on left). Cooling (or heating) produces peaks, which correspond to the transformation temperatures. At higher temperatures, a very sharp increase is observed during cooling through the M_s. These usually high damping characteristics (Ref 22) have been studied for some time, but have not been used on a commercial basis due to their limited temperature range and rapid fatigue degradation.

Elastic Constants

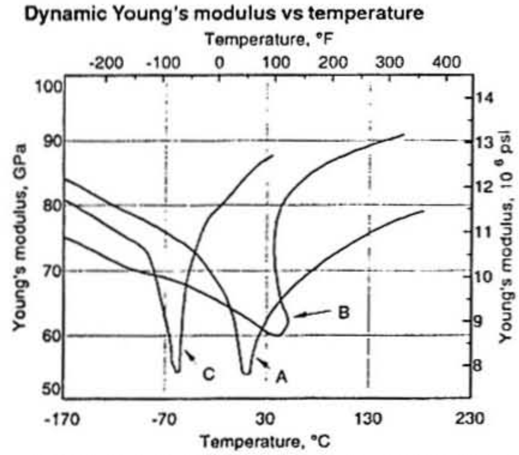
Dynamically measured moduli (Ref 23 and 24) change markedly with the martensitic transformation and premartensitic effects (see figure on right). Typical values of elastic moduli are 40 GPa (5.8×10^6 psi) for martensite and 75 GPa (10.8×10^6 psi) for austenite. From a practical point of

Ti-Ni-Cu alloy damping characteristics



Internal friction of 44.7Ti-29.3Ni-26 Cu (wt%) during cooling with measurement frequency of ~1 Hz.
Source: O. Mercier and E. Török, *J. Phys.*, Vol C-4 (No. 43), 1982, p C-4270

Dynamic Young's modulus vs temperature



A: Ti-55Ni (wt%). B: 44.7Ti-29.3Ni-26Cu (wt%). C: 44.9Ti-51.7Ni-3.4Fe (wt%).
Source: O. Mercier, K.N. Melton, R. Gotthardt, and A. Kulik, *Proc. Int. Conf. Solid-Solid Phase Transformations*, H.I. Aaronson, D.E. Laughlin, R.F. Sekerka, and C.M. Wayman, Ed., AIME, 1982, p 1259

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