Intermetallic Nickel-Titanium Alloys for Oil-Lubricated Bearing Applications

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March 2009
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Abstract

An intermetallic nickel-titanium alloy, NITINOL 60 (60NiTi), containing 60 wt% nickel and 40 wt% titanium, is shown to be a promising candidate material for oil-lubricated rolling and sliding contact applications such as bearings and gears. NiTi alloys are well known and normally exploited for their shape memory behavior. When properly processed, however, NITINOL 60 exhibits excellent dimensional stability and useful structural properties. Processed via high temperature, high-pressure powder metallurgy techniques or other means, NITINOL 60 offers a broad combination of physical properties that make it unique among bearing materials. NITINOL 60 is hard, electrically conductive, highly corrosion resistant, less dense than steel, readily machined prior to final heat treatment, nongalling and nonmagnetic. No other bearing alloy, metallic or ceramic encompasses all of these attributes. Further, NITINOL 60 has shown remarkable tribological performance when compared to other aerospace bearing alloys under oil-lubricated conditions.

Spiral orbit tribometer (SOT) tests were conducted in vacuum using NITINOL 60 balls loaded between rotating 440C stainless steel disks, lubricated with synthetic hydrocarbon oil. Under conditions considered representative of precision bearings, the performance (life and friction) equaled or exceeded that observed with silicon nitride or titanium carbide coated 440C bearing balls. Based upon this preliminary data, it appears that NITINOL 60, despite its high titanium content, is a promising candidate alloy for advanced mechanical systems requiring superior and intrinsic corrosion resistance, electrical conductivity and nonmagnetic behavior under lubricated contacting conditions.

Introduction

Binary nickel-titanium (NiTi) alloys are in widespread use in the medical and dental industries in applications where their biocompatibility and unique superelastic or Shape Memory Effect (SME) characteristics are readily exploited (Refs. 1 and 2). More recently in the aerospace industry, shape memory alloy activated structures have been proposed and demonstrated for such applications as general flow control, adaptive inlets and nozzles, variable geometry chevrons, variable camber fan blades, and flaps and other hinged components (Refs. 3 and 4). These applications capitalize upon the large reversible strain change inherent in typical near equi-atomic NiTi alloys (containing approximately 55 wt% nickel) and ternary high-temperature shape memory alloys (HTSMA) even when opposed by some large force. In addition to these familiar SME alloys, nickel rich alloys, containing approximately 57 to 60 wt% nickel, are also being pioneered for use in adaptive aeronautical systems by Boeing (Ref. 5), and have culminated in a full-scale flight test of NITINOL 60 variable geometry chevrons (Ref. 6).

Unlike more conventional NiTi alloys, the Ni-rich alloys require complicated multistep heat treatments before they are capable of displaying shape memory behavior (Ref. 7). In the present paper, we present, for the first time, evidence that NiTi alloys can be tailored to avoid shape memory or superelastic behavior and that such alloys display excellent tribological properties under oil-lubricated contact conditions.
The NiTi family of alloys traces their origins to pioneering work of William J. Buehler and his colleagues at the Naval Ordinance Laboratory during the late 1950s (Refs. 8 and 9). In fact, the designation NITINOL often used for these alloys is an abbreviation for Nickel-Titanium Naval Ordinance Laboratory. At that time, research was underway to develop high temperature, nonmagnetic alloys for missile cone applications. Their early efforts identified both the NITINOL 55 and NITINOL 60 alloys, which contained 55 and 60 wt% nickel respectively. NITINOL 55 was softer and found to be easier to mechanically work and form than NITINOL 60 which was prone to excessive work hardening. Several hand tools were fabricated from NITINOL 60 to take advantage of its high hardness, electrical conductivity, nonmagnetic behavior and corrosion resistance. These tools were envisioned for use in disarming explosive devices but production did not progress beyond the laboratory stage. Because their resources were limited and the SME properties of NITINOL 55 were so intriguing, research on NITINOL 60 was abandoned by the early 1960s (Ref. 10). Since then, others have attempted to develop methods to produce NITINOL 60 for structural and mechanical applications, such as rolling element bearings (Ref. 11), but for now, it appears that commercial success has been elusive.

Materials for high performance bearings, gears and other mechanical components require a number of specific properties and characteristics. Among these key attributes are high strength and hardness, high thermal conductivity, and the ability to be manufactured to very high levels of precision with regards to final dimensions and surface finish. In addition, excellent corrosion resistance and good tribological properties are often of importance especially for applications in extreme environments.

In rotorcraft, for instance, engine bearings, rotor mechanisms and drive systems are obvious examples where improved corrosion resistance is a benefit. Flight and water vehicles exposed to marine environments are also prone to corrosion related failures despite the widespread use of lubricants with corrosion inhibitors. Even spaceflight hardware destined to operate in the vacuum of space, beyond the realm of atmospheric corrosion, often must be stored for extended periods before launch, and are subject to bearing and gear corrosion problems. In select applications involving electric machines and sensitive instrumentation, good electrical conductivity and nonmagnetic properties can also be highly desirable. Unfortunately, no currently deployed material possesses all of these properties.

Traditional tool steel based bearing materials, such as M50 and 52100 enjoy widespread application due to their high hardness, ease of manufacture and good tribological properties. However, these alloys suffer from corrosion attack if not protected and though electrically conductive they are also highly magnetic. In addition, when used as bearing rolling elements, their high density leads to high centrifugal forces and limited fatigue life. These considerations have driven the search and development of alternate bearing and mechanical component alloys, namely stainless steels and ceramics.

Stainless steels such as 440C are widely used in the bearing and gear industry where corrosion resistance and high hardness are required. These martensitic stainless steels are reasonably low cost, easy to machine prior to heat treatment and are dimensionally stable. When prepared through vacuum melting processes, they achieve very uniform, fully dense microstructures which lead to fine surface finishes and good fatigue behavior. Despite being referred to as stainless, however, the 400 series martensitic steels are prone to corrosion and are more accurately referred to as corrosion-resistant alloys rather than stainless. They are also highly magnetic which can be problematic in certain applications.

Silicon nitride ceramics, on the other hand, are essentially corrosion proof. They can be polished to very fine surface roughness and are quite wear resistant. Silicon nitride’s low density compared to steels also makes it ideal for ultra high-speed applications because lower centrifugal stresses result. These attributes make silicon nitride the material of choice for high stiffness, high load, high-speed bearings and for applications that include corrosive conditions and aggressive sliding environments. Such applications include bearings for gas turbine hot sections, cryogenic oxidizer turbopumps and components for diesel engine fuel injection systems. Though nonmagnetic, silicon nitride is an electrical insulator. It is also more expensive to manufacture than steels owing to the complexity and cost of the high temperature, high pressure powder metallurgy processing required. Silicon nitride’s low thermal expansion coefficient can present challenges in applications involving wide temperature variations.
This paper assesses the feasibility of using NITINOL 60 for bearings and mechanical components. NITINOL 60 offers a unique combination of properties that are not found in any other commonly recognized material. NITINOL 60, when appropriately heat-treated, does not exhibit SME properties at normal ambient and anticipated use temperatures and is dimensionally stable. It has high hardness when properly heat-treated and yet can be readily machined prior to final heat treatment. Like silicon nitride, NITINOL 60 is nonmagnetic and is intrinsically highly resistant to corrosion. Unlike ceramics, NITINOL 60 is electrically conductive. Table I contains a summary of key material properties for conventional and high performance bearing alloys in current use and, for comparative purposes, includes basic properties for NITINOL 55 and NITINOL 60 alloys. Based upon these characteristics NITINOL 60 appears to be an excellent candidate material for bearings provided it performs well in a tribological environment.

<table>
<thead>
<tr>
<th>Property</th>
<th>60NiTi</th>
<th>55NiTi</th>
<th>440C</th>
<th>Si₃N₄</th>
<th>M-50</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density, g/cc</td>
<td>6.7</td>
<td>6.5</td>
<td>7.7</td>
<td>3.2</td>
<td>8.0</td>
</tr>
<tr>
<td>Hardness</td>
<td>56 to 62 RC</td>
<td>35 to 40 RC</td>
<td>58 to 62 RC</td>
<td>1300 to 1500 Hv</td>
<td>60 to 65 RC</td>
</tr>
<tr>
<td>Thermal conductivity W/m-°K</td>
<td>18</td>
<td>9</td>
<td>24</td>
<td>33</td>
<td>~36</td>
</tr>
<tr>
<td>Thermal expansion ~10×10⁻⁶/°C</td>
<td>~10×10⁻⁶/°C</td>
<td>10×10⁻⁶/°C</td>
<td>2.6×10⁻⁶</td>
<td>~11×10⁻⁶/°C</td>
<td></td>
</tr>
<tr>
<td>Magnetic</td>
<td>Non</td>
<td>Non</td>
<td>Mag</td>
<td>Non</td>
<td>Mag</td>
</tr>
<tr>
<td>Corrosion resistance</td>
<td>Excellent</td>
<td>Excellent</td>
<td>Marginal</td>
<td>Excellent</td>
<td>Poor</td>
</tr>
<tr>
<td>Tensile/flexural strength, MPa</td>
<td>aTBD</td>
<td>~900</td>
<td>1900</td>
<td>600 to 1200 (bend strength)</td>
<td>2500</td>
</tr>
<tr>
<td>Young’s modulus, GPa</td>
<td>~114</td>
<td>~100</td>
<td>200</td>
<td>310</td>
<td>210</td>
</tr>
<tr>
<td>Poisson’s ratio</td>
<td>TBD</td>
<td>TBD</td>
<td>0.3</td>
<td>0.29</td>
<td>0.30</td>
</tr>
<tr>
<td>Fracture toughness</td>
<td>TBD</td>
<td>TBD</td>
<td>22 MPa/√m</td>
<td>5 to 7 MPa/√m</td>
<td>20 to 23 MPa/√m</td>
</tr>
<tr>
<td>Maximum use temperature, °C</td>
<td>~400</td>
<td>~400</td>
<td>~400</td>
<td>~1100</td>
<td>~400</td>
</tr>
<tr>
<td>Electrical resistivity</td>
<td>~8×10⁻⁶ Ω-cm</td>
<td>~8×10⁻⁶ Ω-cm</td>
<td>~36×10⁻⁶ Ω-cm</td>
<td>Insulator</td>
<td>~6×10⁻⁶ Ω-cm</td>
</tr>
</tbody>
</table>

aTBD means to be determined.

Historically, metallic alloys with high concentrations of titanium are poor tribological materials in that they do not respond well to lubrication by organic fluids (Ref. 12). For instance, alloys such as Ti-6Al-4V exhibit galling behavior in dynamic contacts even under conditions well lubricated by oils and greases. During contact, titanium readily transfers to the counter-face leading to rough surfaces, high friction and wear. In addition, titanium alloys are recognized as being chemically aggressive causing degradation of many lubricants (Ref. 12). When titanium alloys must be used due to other attributes like high specific strength or corrosion resistance, tribological contact is avoided through the use of thick barrier coatings and claddings. Based upon a wealth of negative experience with titanium alloys in tribological contacts, NITINOL 60 would appear an unlikely candidate as a bearing material.

On the other hand, ceramic materials with high concentrations of titanium can exhibit desirable tribological properties. Titanium carbide (TiC) and titanium dioxide (TiO₂) are good examples. TiC coatings are often used to improve the surface finish and performance of stainless steel rolling elements in bearings and TiO₂, in the form of rutile, has been put forth as a potential solid lubricant under certain conditions (Refs. 13 and 14). These ceramic materials, however, are brittle and cannot be used as structural elements.

If bond strength or some other nature of the bonding in Ti-based materials has a significant effect on tribological behavior then it is not clear how NITINOL 60 may tribologically perform. NiTi is a Hume-Rothery β-phase electron compound with a valence electron to atom ratio of 3:2, which gives rise to the
stability of a large number of ordered intermetallic alloys that crystallize in the (B2) CsCl structure with components of both metallic and covalent bonding (Ref. 15). Compared to ceramics like TiC and TiO2, B2 NiTi is much less covalent and thus expected to show more toughness, ductility, and chemical reactivity. But compared to more common metallic alloys like Ti-6Al-4V, the bonding between the Ni and Ti is highly directional and much stronger and may therefore share tribological properties with the ceramics. In spite of these considerations, there is presently no understanding at the fundamental level of why metallic titanium alloys perform so poorly under lubricated tribological conditions. A consideration of NITINOL 60 as a tribological material thus requires an experimental study of its performance in a lubricated configuration.

The existing patent literature purports that NITINOL 60, in cast form, is a good bearing material, even in un-lubricated contacts, though no supporting data is provided (Ref. 11). Limited dry sliding tests of NITINOL 60 indicated rather high friction (Ref. 16). Studies on the dry sliding behavior of the more common SME alloy NITINOL 55 are sparse but the data indicate that like the NITINOL 60, friction coefficients in dry sliding are high, typically well above 0.5 (Ref. 17). A very recent paper describing the tribological behavior of NITINOL 55 in fretting and corrosion conditions designed to simulate in vivo applications corroborates earlier findings that sliding friction and wear levels are high under unlubricated conditions (Ref. 18). There appears to be no published examples for the tribological performance of any NITINOL alloys in lubricated contacts. Furthermore, to the authors’ knowledge, NITINOL 60 has never been evaluated in the presence of a lubricant nor has it ever been evaluated under conditions simulative of a bearing application.

Consequently, the present investigation seeks to determine whether NITINOL 60 is a promising candidate material for tribological applications such as bearings. First, aerospace quality NITINOL 60 bearing balls were manufactured via a powder metallurgy processing route. Cross-section metallographic analyses were undertaken to characterize the material microstructure and its basic composition and selected mechanical properties were estimated or determined. Then, a series of rolling-sliding tests were performed under oil-lubricated conditions simulative of an aerospace ball bearing. Finally, after direct comparisons were made with conventional bearing materials, an assessment is provided on the likelihood of employing NITINOL 60 for mechanical components.

Materials

The 60NiTi evaluated in this work was manufactured via a high temperature proprietary powder metallurgy process roughly similar to that described in the literature (Ref. 19). Pre-alloyed 60NiTi powder was HIPed into rough, spherical ball blanks that were then ground, polished, and lapped to produce high quality (Grade 5) bearing balls 0.5 in. (12.5 mm) in diameter. A multistep thermal process (heat treatment) was used to enable rough grinding of the bearing balls in a softened state followed by lapping to a very fine surface finish in a final hardened condition. The finished 60NiTi ball specimens, shown in the photograph in Figure 1, are bright and shiny in appearance and resemble conventional polished steel balls.

The elemental composition of the bearing material, as measured by atomic emission spectroscopy and energy dispersive, semi-quantitative x-ray analysis, were consistent and showed the balls are nominally 55 at.% nickel with the balance titanium. This translates to 60 wt% nickel, 40 wt% titanium, hence the historical designation of 60NiTi. Density was measured at 6.71 g/cc and is about 25 percent lower than 440C stainless steel.

Figure 2 shows the cross sectional microstructure of the 60NiTi specimens in the final hardened and polished condition. Microhardness measurements indicate values in the range of 58 to 62 on the Rockwell C scale in the hardened condition. As with most HIPed or sintered powder compacts, the prior particle boundaries are quite evident and are delineated by oxides and other tramp phases. Despite containing only Ni and Ti, Ni-rich NITINOL microstructures can be very complex due to a series of metastable intermetallic phases that could exist depending on thermal history (Ref. 20). Analysis of the 60NiTi ball specimens reveals multiple discrete phases. These are shown in Figure 3.
Figure 1.—Photograph of 60NiTi polished ball specimens prior to testing.

Figure 2.—Cross-section photomicrograph of 60NiTi ball showing grain structure typical for powder metallurgy processed materials.
Figure 3.—(a) High magnification micrograph and corresponding area image analysis. (Outlined box shows analyzed area). (b) Area image analyses of 60NiTi cross section showing discrete phases and their relative proportions based upon area fraction.
A combination of x-ray diffraction analyses, energy dispersive spectroscopy and orientation image microscopy has been used to identify the phases present. The dominant phase is B2-structured NiTi and is considered the bulk phase appearing at about a 78 percent volume fraction, based upon two-dimensional image area analyses. It is a continuous phase broken up by other tramp phases that delineate the prior particle boundaries. The second most predominant phase appears as narrow, rod shaped regions, several microns long and about a half micron in diameter and is dispersed throughout the bulk NiTi phase at a concentration of ~11 vol%. Analyses indicate it is Ni<sub>4</sub>Ti<sub>3</sub>, which is a relatively fine metastable phase observed in low temperature aged or slow cooled Ni-rich NiTi alloys. A third phase making up about 9 percent of the material, appearing as irregularly shaped regions, concentrated at the grain boundaries or prior particle boundaries, was found to be Ni<sub>3</sub>Ti. This equilibrium phase generally appears after aging at high temperatures and long times and depending on the volume fraction present is partly responsible for controlling the temperature at which any shape memory properties might be observed. At higher volume fractions, it also leads to softening of the alloy making rough machining during intermediate processing steps easier to accomplish. The fourth phase observed was Ti<sub>3</sub>Ni. This is a tramp intermetallic phase that forms during solidification of the powder particles and has a high solubility for oxygen. It is generally segregated at grain or prior particle boundaries and occurs at less than about 2 vol.%. Continued microstructural analysis of the 60NiTi is underway to corroborate the functional contributions of each phase to the mechanical and potentially the tribological properties of the alloy.

Preliminary differential scanning calorimetry (DSC) results are shown in Figure 4 for the bearing blanks and finished bearings and compared to the typical behavior of 55NiTi. The results suggest that the 60NiTi bearing blanks may have a slight amount of martensite that could form if cooled below –15 °C. However, the final hardened bearings are microstructurally stable down to at least –100 °C. Figure 5, which is a compilation of data from several studies from the literature (Refs. 21 to 23) corroborates this preliminary assessment and shows that others have found that the martensite transition temperature drops precipitously below room temperature for quenched nickel rich NiTi alloys.

Figure 4.—DSC behavior of the bearing blank material in the softened condition and hardened and polished 60NiTi bearing ball material shown in comparison to conventional 55NiTi shape memory alloy. As expected, the 60NiTi specimens tested in this study exhibit little phase transition behavior.
Tribological Evaluation

For the tribological evaluation, 60NiTi ball specimens were lubricated with a thin film of synthetic hydrocarbon oil named Pennzane (Ref. 24), and subjected to a rolling-sliding contact lubricant wear life test in a Spirol-Orbit-Tribometer (SOT). The paragraphs that follow more fully describe both the lubricant and the SOT tribological test system.

The SOT is depicted in Figures 6 and 7 and described in detail in References 13 and 25. It is basically a thrust bearing with one ball and flat races (plates). It may be regarded as a simplified version of the usual angular contact ball bearing. One of the plates is stationary and the other rotates to drive the ball into an orbit that is an opening spiral. The ball contacts a guide plate at the end of each orbit, which forces the ball back into its initial orbital radius. The ball then exhibits, for a given coefficient of friction (CoF), a stable orbit, repeatedly over-rolling the track on both flat race plates and guide plate. The spiral’s pitch and the length of the contact on the guide plate increases with the increase in the CoF. A piezoelectric force transducer supporting the guide plate senses the frictional force developed on the ball as it slides on the rotating plate during the contact of the ball with the guide plate. During this contact, the coefficient of friction is obtained from this force and the load imposed on the system. The tribometer is housed in a stainless steel chamber that can be evacuated by a turbomolecular pump to ≤2×10⁻⁸ torr. It can be operated either in this vacuum environment or at atmospheric pressure.

Figure 5.—Effects of Ni-Ti ratio on the martensitic transition temperature demonstrating that at high Ni-contents the martensitic transformation is suppressed to very low temperatures. This implies high dimensional stability for the 60NiTi alloy.
Figure 6.—Spiral orbit tribometer used to evaluate the relative lubricant life of various alloys under simulated bearing conditions.

Figure 7.—Components of the spiral orbit tribometer (SOT). The top plate and guide plate are stationary, while the bottom plate rotates to drive the ball.
The plate specimens were 440C stainless steel. They were lapped flat and their final polish resulted in an arithmetic mean surface roughness, $R_a < 25$ nm (1 μin.) determined by optical interferometry. The 60NiTi balls were 12.7 mm (0.5 in.) diameter, Grade 5. The final surface cleaning procedure for all ball and plate specimens was by lightly rubbing with aqueous slurries of silicon carbide polishing powders, followed by sonication in deionized water. This preparation results in a surface on which water exhibits zero contact angle (spreads) and which exhibits an XPS spectrum (a) devoid of impurities other than a small feature due to adventitious carbon and (b) in which the Fe$^0$ feature in the 440C steel is clearly evident, indicting a native oxide to be approximately 2 nm thick.

The plates were initially clean and only the ball was lubricated. For the present tests in the boundary regime, the ball is first weighed and then lubricated by dripping a dilute solution of the lubricant, ~1 μg of lubricant per μl of hexane solvent, onto the ball rotating on a small bench lathe. The ball is reweighed after evaporation of the solvent and the lubricant charge is obtained from the weight difference. About 20 μg (24 nl) of lubricant were used on the ball.

The lubricant chosen for testing with the 60NiTi balls was a multiply alkylated cyclopentane (MAC) designated by the trade name Pennzane 2001A. This oil, containing only carbon and hydrogen in its structure, is a mixture of di- and tri-substituted (2-octyldodecyl) cyclopentane. It is described more fully in Reference 25 and a sketch of its structure is shown in Figure 8.

![Molecular structure of the lubricant used in the SOT tests.](image)
The elastic modulus of 60NiTi is not presently known. Tests were run here at a system load of 30 lb, which resulted in a track width of ~0.4 mm. This track width is close to that resulting from a test with a 440C steel ball at a load of 43 lb, which corresponds to a Hertz pressure of 1.5 GPa at the ball/plate contact. The 30 lb load in the Nitinol tests corresponds to a Hertz pressure of 1.06 GPa. Such a Hertz pressure is obtained if the 60NiTi material has an elastic modulus of 114 GPa, which is comparable to that of the Ti-6Al-4V alloy.

In tests in the SOT with only µg’s of lubricant, the system is obviously operating in the boundary regime of lubrication. The characteristic of a test in which boundary lubrication is operative is a low and constant coefficient of friction (CoF) for a number of orbits and then an eventual transition to a much higher value of the CoF. This eventual increase has been attributed to the consumption of the organic lubricant by tribochemical attack on the lubricant molecules in the ball/plate contact by the bearing materials between which the lubricant is captured. Each member of the ball/plate contact can exhibit tribochemical activity that degrades molecular structure, consuming the lubricant and leading to high CoF in the absence of lubricant and the end of the test. In a symmetric system, 440C steel/440C steel for example, each member in the ball/plate contact contributes equally to the tribochemical attack rate and a typical lifetime (orbits to failure per µg of lubricant initially applied) is obtained. Figure 9 displays the friction versus number of cycles for the standard 440C ball operating against 440C plates. As expected, the friction is low and stable until the lubricant is depleted whereupon the friction rises and the test is terminated.

In the asymmetric system considered here where each member of the contact may have different tribochemical activities, smaller or greater lifetimes may occur. An extreme case is one in which one of the partners exhibits such great tribochemical aggressiveness that the lubricant does not survive the contact at all and failure of the lubrication is immediate, with no observable lifetime. The other extreme case is that in which one of the partners exhibits no tribochemical activity at all and the test’s (longer) lifetime is determined only by the activity of the other partner. The goal in this report is provide a first assessment of the ability to lubricate the 60NiTi via vacuum SOT tests with the 60NiTi/440C steel/oil system.

![Graph showing friction versus orbit number for 440C steel ball lubricated with 16 µg Pennzane 2001A running on 440C steel plates.](image)

**Figure 9.**—Typical SOT friction trace for 440C ball and disks lubricated with small volume of oil.
Tribology Test Results

Determination of the ability of 60NiTi to be lubricated is best illustrated by first referring to a test of Pennzane 2001A on specimens that are all 440C steel. This is an oil/metal combination that is well established as a system that can be successfully lubricated. The friction trace of a typical test shown in Figure 9 illustrates the characteristics referred to in the previous section—a low constant coefficient of friction (CoF) for the first ~10,000 orbits, followed by an eventual increase of the CoF to high values associated with the failure of lubrication due to the absence of lubricant.

The sensitivity of the SOT test to the surface chemical constitution of the ball is illustrated in Figure 10 in which two friction traces are shown. One is the initial stage of the test with a 440C steel ball whose friction trace is shown in Figure 9, while the other is a test of a 440C ball coated with a thin film of titanium. Both balls had been lubricated with Pennzane 2001A and run on 440C steel plates in vacuum. It is evident from the high erratic CoF of the test with the titanium-coated ball that the system is not operating in a lubricated manner. This is attributed to the destruction of the Pennzane’s molecular structure and attendant loss of lubrication capability by the tribochemically aggressive titanium film with which it is in contact. This test demonstrates that only one partner of a tribological pair needs to be tribochemically aggressive to prevent effective lubrication. Such highly aggressive tribochemical behavior was also observed with a 60NiTi ball coated with titanium, so that the effect is not dependent on the particular mechanical properties of the ball, but is really of chemical origin. Figure 10 illustrates the extreme cases within which a test of the capability of lubricating a particular material falls—lubrication, indicated by low and constant CoF and lack of lubrication, indicated by high and erratic CoF.

![Friction traces of a system with a 440C steel ball and a 440C steel ball coated with a thin film of titanium. Both balls have been lubricated with ~25 µg of Pennzane oil and run on 440C steel plates.](image-url)
The friction trace of a test with a 60NiTi ball lubricated with Pennzane 2001A and running on 440C plates is shown in Figure 11. The trace exhibits the same characteristics of the trace for the Pennzane/all-440C steel system shown in Figure 9. There is low constant initial CoF that gradually increases to the high values resulting from the consumption of lubricant by tribochemical attack. The initial stage of friction traces comparing the all-steel system to the system with the 60NiTi ball running on 440C steel plates is shown in Figure 12. This figure illustrates the similarity of the behavior of the CoF for the two systems, although the system with the 60NiTi ball exhibits somewhat lower initial values of the CoF. All tests with the 60NiTi balls running on 440C steel plates exhibited this behavior. It is thus concluded that 60NiTi can be effectively lubricated by the popular lubricant Pennzane 2001A.
The friction traces of the asymmetric system with the 60NiTi ball generally exhibited lower initial friction, but subsequent lubricant depletion resulted in failure at fewer orbits than the symmetric system with the 440C steel ball. The number of orbits to achieve CoF=0.2 divided by the lubricant charge in μg is termed the normalized lifetime to characterize the system’s tribochemical aggressiveness. Shorter normalized lifetime implies greater tribochemical aggressiveness. The normalized lifetime for any given system does exhibit variability. Table 2 presents normalized lifetimes and initial CoFs obtained in the SOT for the symmetric and asymmetric systems under consideration here. The asymmetric system with 60NiTi ball exhibits somewhat shorter lifetimes than does the symmetric system with the 440C steel ball, suggesting that 60NiTi is somewhat more tribochemically aggressive than is 440C steel. However, note that the tests with the 60NiTi ball were performed at the lower Hertz pressure of 1.06 GPa compared to the higher Hertz pressure of 1.5 GPa at which the 440C steel balls were run. Thus the comparison is not completely direct and the relative degree at which 60NiTi attacks Pennzane 2001A remains to be better determined. However, whatever its degree, it is clear that effective lubrication of 60NiTi is routinely observed.

<table>
<thead>
<tr>
<th>Normalized lifetime, orbits/μg</th>
<th>440C Ball</th>
<th>60NiTi Ball</th>
</tr>
</thead>
<tbody>
<tr>
<td>1981</td>
<td>2302</td>
<td>1347</td>
</tr>
<tr>
<td>1429</td>
<td>1024</td>
<td>836</td>
</tr>
<tr>
<td>Initial CoF</td>
<td>0.079</td>
<td>0.079</td>
</tr>
<tr>
<td></td>
<td>0.081</td>
<td>0.061</td>
</tr>
<tr>
<td></td>
<td>0.062</td>
<td>0.059</td>
</tr>
</tbody>
</table>

Finally, Figure 13 shows a friction trace of a test for which the CoF was allowed to exceed the nominal cutoff value of 0.3 and kept running into the failure region. The system is observed not to gall and seize up, but instead to continue to run, albeit with a high CoF of 0.3 to 0.4. Figure 14 shows a micrograph of the 60NiTi ball surface after this test. It is worn but does not show signs of galling or material buildup and transfer. It thus appears that 60NiTi/440C steel system fails gracefully without the self-destructive seizure characteristic of many all-steel tribosystems.

![Friction trace of a Pennzane P2001A/Nitinol 60/440C steel system running in vacuum and continued until failure.](image)
Discussion

NiTi alloys enjoy widespread use in applications where their shape memory or superelastic properties are considered desirable. Most of these applications are relatively static, for instance vascular stents and dental implant wire, and do not experience any sliding or tribological contact. In fact, though several patents have been awarded for Nitinol bearings, very little research has ever been reported on their tribological properties. Kolbe and Zum Gahr (Ref. 17) reported on the friction and wear of 55NiTi under dry sliding conditions using a pin-on-disk apparatus in 1998. Their work was motivated by the desire to determine the suitability of using the more common shape memory alloy NiTi in mechanical biomedical device applications such as flexible endoscopes. They found friction to be high under dry sliding but observed none of the galling tendencies exhibited by pure titanium and nickel sliding tribopairs.

More recently, Miyoshi and his colleagues conducted similar dry sliding tests of the 60NiTi alloy under vacuum conditions to determine feasibility for use in nonspecified aerospace applications (Ref. 16). Though the tests were carried out at room temperature, anticipated applications included elevated temperature conditions that precluded the use of oils and conventional solid lubricants. Miyoshi’s results for 60NiTi generally corroborated the earlier findings of Kolbe and Zum Gahr. Under dry sliding conditions, the NiTi alloys exhibit mild abrasive wear tendencies without the galling behavior normally associated with metallic titanium alloys (Ref. 12). Despite the existence of Nitinol alloys for over four decades, it appears that no lubricated tribology tests have ever been conducted until the present study.

The lack of lubricated test experience for NiTi alloys is, in retrospect, not surprising. Most current applications of NiTi are biomedical and the presence of oil or grease lubricant would be medically problematic. Emerging applications for NiTi shape memory alloys include a replacement for conventional actuators, such as hydraulic, pneumatic or motor-based systems in adaptive aerostructures and by design do not incorporate any sliding contacts (Refs. 3 to 6). The apparent lack of contacting surfaces, when used in actuating settings, may explain why there has been little driving force for investigating the tribological properties of NiTi alloys under lubricated conditions. Further, the patent literature makes claims that NiTi alloys do not require additional lubricants for tribological applications and may actually be lubricated by salt water (Refs. 11 and 26). No supporting data is given but such unsubstantiated performance claims may have also contributed to the absence of lubricated tribology data for NiTi alloys. A more important
factor may be that NiTi alloys are generally exploited for their ability to change shape, whether in terms of shape memory characteristics or superelasticity, and such variable geometry makes their use in bearings and mechanical components difficult.

On the other hand, recent patents indicate that with proper thermal and mechanical processing, the properties of NiTi alloys of varying composition can be readily controlled (Refs. 11, 27, and 28). These controllable properties appear to include hardness, ductility and transition temperature. In other words, NiTi alloys can be tailored in such a manner as to suppress any transformation to martensite outside the intended use application, thus assuring dimensional and microstructural stability over the range of application for typical bearing elements. Since the transition temperature for the 60NiTi bearing material studied here is estimated to be well below –100 °C, shape memory behavior is not relevant.

An interesting parallel could be drawn between the Ni-Ti materials system and the one based upon iron and carbon, Fe-C. Figure 15 shows the basic Fe-C phase diagram. Compositions containing small amounts of carbon, when properly processed and heat treated, yield tough, hard steel alloys. Higher carbon containing materials conversely are observed as soft grey cast irons and as hard white cast irons. It has only been through the centuries of dedicated experimental and analytical investigations that a complete picture of the property-composition-processing relationships for the Fe-C system has been revealed. The Ni-Ti system may well offer a similar complexity belying its apparent simplicity.

Figure 15.—Fe-C binary phase diagram.
Figure 16 shows the phase diagram for the Ni-Ti system with callouts at both the 55NiTi and 60NiTi compositions. These alloys have widely varying properties and thus differ in their applicability to engineering uses. Though they share similar metallurgy, the more equi-atomic 55NiTi is relatively soft and displays remarkable shape memory effects; the nickel rich 60NiTi can be thermally treated to behave similar to 55NiTi or conversely can be processed in a manner that essentially suppresses the martensitic transformation and hardens the alloy to such an extent that fracture can occur simply from rapid cooling. In between, 60NiTi can be processed in a manner that yields a fine-grained structural material with high hardness that can be polished to smooth surface finish yielding excellent lubricated tribological properties. Thus the Ni-Ti binary system may contain hidden characteristics that have only recently begun to be revealed and understood.
Summary Remarks

This research effort has identified NITINOL 60 as a promising candidate material for bearing and mechanical component applications. NITINOL 60, when appropriately processed and fabricated, is dimensionally stable, hard, wear resistant, nongalling, and tribochemically benign in the presence of liquid lubricants. This behavior is in stark contrast to conventional alloys that contain such large amounts of the metal titanium. It is believed that the good tribological performance under oil lubrication observed for NITINOL 60 may extend to the entire NiTi family of alloys since they all share similar phase constituents and basic atomic level bonding. The tribochemistry of NITINOL 60 and its metallurgical relatives is under further study.

The identification of a viable bearing material that is nonmagnetic, electrically conductive, hardenable, displays favorable tribochemistry and is noncorrosive is a major research finding. No other bearing material yet discovered has such a broad combination of properties. While it is clear that near term niche applications such as aerospace bearings and gears exist, many nonobvious applications are also likely to present themselves. These include wear resistant, corrosion proof knives and cutters, electric machine structural and dynamic components, high performance fasteners, valve components and many others.

Clearly, much more research will be required to understand the NITINOL 60 material and its metallurgical relatives. The relationships between mechanical and physical properties, atomic structure and micro-scale ordering and surface chemical interactions remain to be investigated. Nonetheless, the NiTi metallurgical system clearly has engineering potential well beyond shape memory alloy applications that has only begun to be exploited.

References

An intermetallic nickel-titanium alloy, NITINOL 60 (60NiTi), containing 60 wt % nickel and 40 wt % titanium, is shown to be a promising candidate material for oil-lubricated rolling and sliding contact applications such as bearings and gears. NiTi alloys are well known and normally exploited for their shape memory behavior. When properly processed, however, 60NiTi exhibits excellent dimensional stability and useful structural properties. Processed via high temperature, high-pressure powder metallurgy techniques or other means, 60NiTi offers a broad combination of physical properties that make it unique among bearing materials. 60NiTi is hard, electrically conductive, highly corrosion resistant, less dense than steel, readily machined prior to final heat treatment, nongalling and nonmagnetic. No other bearing alloy, metallic or ceramic encompasses all of these attributes. Further, 60NiTi has shown remarkable tribological performance when compared to other aerospace bearing alloys under oil-lubricated conditions. Spiral orbit tribometer (SOT) tests were conducted in vacuum using 60NiTi balls loaded between rotating 440C stainless steel disks, lubricated with synthetic hydrocarbon oil. Under conditions considered representative of precision bearings, the performance (life and friction) equaled or exceeded that observed with silicon nitride or titanium carbide coated 440C bearing balls. Based upon this preliminary data, it appears that 60NiTi, despite its high titanium content, is a promising candidate alloy for advanced mechanical systems requiring enhanced corrosion resistance, electrical conductivity and non-magnetic behavior under lubricated contacting conditions.