Nickel-Titanium Alloys: Corrosion "Proof" Alloys for Space Bearing, Components and Mechanism Applications

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Abstract

An intermetallic nickel-titanium alloy, 60NiTi (60wt%Ni, 40wt%Ti), is shown to be a promising candidate tribological material for space mechanisms. 60NiTi offers a broad combination of physical properties that make it unique among bearing materials. 60NiTi is hard, electrically conductive, highly corrosion resistant, readily machined prior to final heat treatment, and is non-magnetic. Despite its high titanium content, 60NiTi is non-galling even under dry sliding. No other bearing alloy, metallic or ceramic, encompasses all of these attributes. Since 60NiTi contains such a high proportion of titanium and possesses many metallic properties, it was expected to exhibit poor tribological performance typical of titanium alloys, namely galling type behavior and rapid lubricant degradation. In this poster-paper, the oil-lubricated behavior of 60NiTi is studied.

Introduction

Binary Nickel-Titanium (Ni-Ti) alloys are in widespread use in the medical and dental industries in applications where their biocompatibility and unique superelastic or Shape Memory Effect characteristics are readily exploited [1]. The Ni-Ti family of alloys traces their origins to pioneering work of William J. Buehler and his colleagues at the Naval Ordnance Laboratory during the late 1950's [2,3]. The designation NITINOL often used for these alloys is an abbreviation for Nickel-Titanium Naval Ordnance Laboratory. Buehler's early efforts identified both the Nitinol 55 and Nitinol 60 alloys, which contained 55 and 60 weight percent nickel respectively. Nitinol 55 is soft and was found to be easier to mechanically work and form than Nitinol 60 that was prone to excessive work hardening. Several hand tools were fabricated from Nitinol 60 to take advantage of its high hardness, electrical conductivity, non-magnetic behavior and corrosion resistance [4].

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. 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 non-magnetic 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.

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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.

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, and 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 non-magnetic, 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. Another shortcoming of silicon nitride is the difficulty of fabricating it into bearing raceways and other complex geometries.

Historically, metallic alloys with high concentrations of titanium are poor tribological materials in that they do not respond well to lubrication by organic fluids [5]. 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 [6]. 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, 60NiTi 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 (TiO_2) are good examples. TiC coatings are often used to improve the surface finish and performance of stainless steel rolling elements in bearings and TiO_2, in the form of rutile, has been put forth as a potential solid lubricant under certain conditions [6, 7]. These ceramic materials, however, are brittle and cannot be used as structural elements. In the present paper, we present evidence that hardened NiTi alloys can be produced that are devoid of shape memory or superelastic behavior and that such alloys display excellent tribological properties under oil-lubricated contact conditions.

Materials and Procedures

The 60NiTi balls evaluated in this work was manufactured via a high temperature proprietary powder metallurgy process roughly similar to that described in the literature [8]. Pre-alloyed 60Ni-Ti 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 inch (12.5 mm) in diameter. 60NiTi plates were cut from cast and hot rolled plate stock. A multi-step thermal process (heat treatment) was used to enable rough machining of the plates and 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 specimens are nominally 55 atomic percent Nickel with the balance titanium. This translates to 60 weight percent Nickel, 40-weight percent titanium, hence the historical designation of NITINOL 60 or 60NiTi. Density was

measured at 6.71 g/cc and is about 15% lower than 440C stainless steel. Table I displays known and estimated properties of 60NiTi.


Figure 1. Nitinol 60 grade 5 test balls.

Table I. Nominal Comparative properties for conventional bearing alloys and NiTi55 and 60NiTi Nitinol 60 grade 5 test balls.					
Property	NiTi-60	NiTi-55	440C	Si3N4	M-50
Density	6.7 g/cc	6.5 g/cc	7.7 g/cc	3.2 g/cc	8.0 g/cc
Hardness	56-62 Rc	35-40 Rc	58-62 Rc	1300-1500Hv	60-65Rc
Thermal Conductivity W/m-°K	18	9	24	33	~36
Thermal Expansion	~10x10-6/°C	~10x10-6/°C	10x10-6/°C	2.6x10-6	~11 10-6/°C
Magnetic	Non	Non	Magnetic	Non	Magnetic
Corrosion Resistance	Excellent	Excellent	Marginal	Excellent	Poor
Tensile/Flexural Strength	~1000MPa	~900 MPa	1900 MPa	600-1200MPa (Bend Strength)	2500 MPa
Young's Modulus	~114 GPa	~100 GPa	200 GPa	310 GPa	210 GPa
Poisson's Ratio	TBD	~.3	.3	.29	.30
Fracture Toughness	TBD	TBD	22 MPa/√m	5-7 MPa/√m	20-23 MPa/√m
Maximum Use Temp	~400° C	~400° C	~400° C	~1100° C	~400° C
Electrical Resistivity	~80x10-6 Ω-cm	~80x10-6 Ω-cm	~36x10-6 Ω-cm	Insulator	~60x10-6 Ω-cm

*TBD means "to be determined"

Figure 2 shows the cross sectional microstructure of the 60NiTi ball specimens in the final hardened and polished condition. Microhardness measurements indicate values in the range of 58-62 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 [9]. Analysis of the 60NiTi ball specimens reveals multiple discrete phases (NiTi,) with NiTi dominating at approximately a 77% volume fraction. The balance is made up from Ni_4Ti_3 at 11%, Ni_3Ti at 10%, and $NiTi_2$ at 2%.
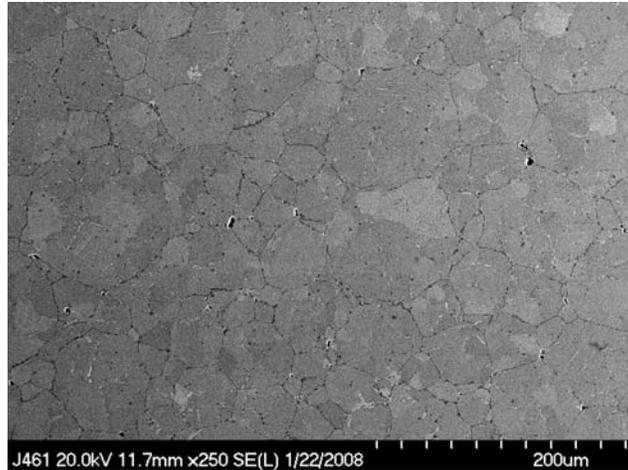
Figure 2. Cross-section electron micrograph of Nitinol 60 ball.

Preliminary differential scanning calorimetry results for the bearing blanks and finished bearings suggest that the 60NiTi bearing blanks may have a slight amount of martensite that could form if cooled below -15°C but in the hardened condition are microstructurally stable down to at least -100 degrees centigrade. This indication is corroborated by our physical measurements of the bearing balls and plates that have been dimensionally stable throughout the processing, handling and research activities undertaken. Buehler also reported excellent stability during the early alloy development [3].

To assess its tribological properties, Spiral Orbit Tribometer (SOT) tests were conducted using a single 60NiTi ball loaded between two rotating disks, lubricated with synthetic oil and tested in a vacuum. In this test, the 60NiTi ball is marginally lubricated with a small quantity (~25 micrograms) of oil and undergoes mostly rolling contact interrupted by a scrubbing/sliding event every disk rotation. The SOT is depicted in Figure 3 and described in detail in references 6 and 10. It is basically a thrust bearing with one ball and flat races (plates). 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. 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 $\leq 2 \times 10^{-8}$ Torr. It can be operated either in this vacuum environment or at atmospheric pressure.

The plate specimens were 440C stainless steel or 60NiTi. They were lapped flat and their final polish resulted in an arithmetic mean surface roughness, Ra, <25 nm (1 min) determined by optical interferometry. The 60NiTi balls were 12.7 mm (.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.

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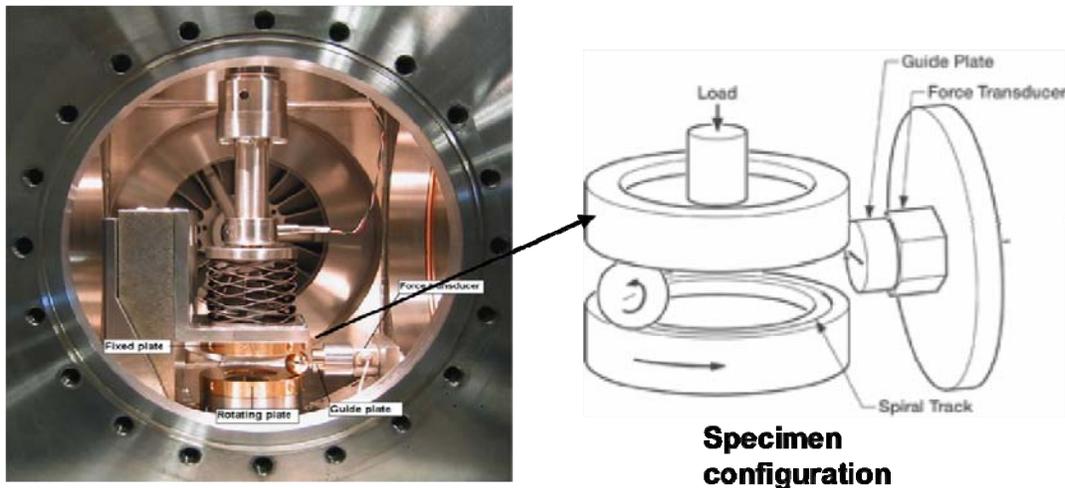
Figure 3. Spiral Orbit Tribometer used to evaluate the relative lubricant life of various alloys under simulated bearing conditions.

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 mg of lubricant per ml 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 mg (24 nl) of lubricant, a multiply alkylated cyclopentane (MAC) designated by the trade name Pennzane 2001A, were used on each ball. Tests were run here at a system load of 130 N (30 lb), which resulted in a track width of ~0.4 mm and corresponds to a Hertz pressure of 1.06 GPa. The test conditions result in operation in the boundary lubrication regime. Considering the small quantity of lubricant present in the tribosystem, test lifetimes on the order of a few tens of thousands are typical for good tribological materials like 440C and past experience with the SOT indicate its relevance in mimicking the conditions in a space ball bearing application [6].

Results and Discussion

Under these conditions considered representative of precision bearings, performance (life and friction) was comparable to that observed with 440C bearing balls. Figure 4 shows friction for tests of 60NiTi balls running against 440C plates (left graph) and Nitinol 60 plates (right graph) in the SOT. Typical lubricant lifetimes were approximately 30,000-60,000 revolutions indicating a slow lubricant consumption rate. In one test using both 60NiTi plates and ball, the rig was permitted to run well beyond the complete consumption of lubricant. In that case, friction climbed to a coefficient of around 0.35 but was stable and no galling tendencies were observed.

In comparison, SOT tests of balls sputter coated with pure, thin titanium films degrade the lubricant, experience high friction and seizure within a few dozen revolutions. Unlike traditional titanium alloys, the 60NiTi alloy performs well and is a good candidate for bearings and mechanical components and is impervious to the corrosion issues facing traditional bearing materials especially during storage before launching.
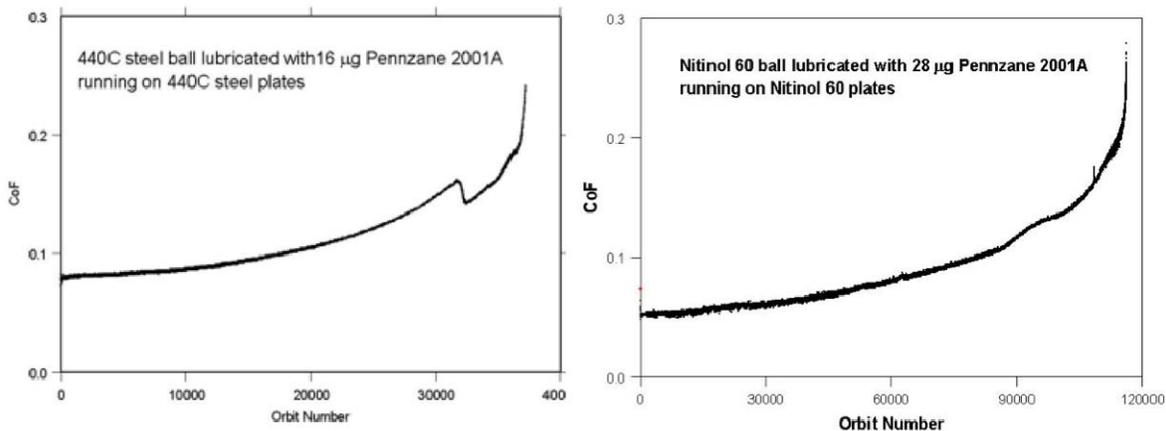
Figure 4. SOT results for Nitinol 60 ball running against 440C (left) and Nitinol 60 plates (right) showing comparable behavior.

Summary

This research effort has identified 60NiTi alloy as a promising candidate material for bearing and mechanical component applications. 60NiTi, when appropriately processed and fabricated, is dimensionally stable, hard, wear resistant, non-galling, 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 60NiTi may extend to the entire NiTi family of alloys since they all share similar phase constituents and basic atomic level bonding. The tribochemistry of 60NiTi and its metallurgical relatives is under further study.

The identification of a viable bearing material that is non-magnetic, electrically conductive, hardenable, displays favorable tribochemistry and is non-corrosive 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 non-obvious 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 60NiTi 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

1. S.A. Shabalovskaya: "Surface, Corrosion and Biocompatibility Aspects of Nitinol as an Implant Material", Bio-Medical Materials and Engineering, volume 12, 2002, 69-109.
2. Buehler, W.J., J.V. Gilfrich, and R.C. Wiley: "Effect of Low-Temperature Phase Changes on the Mechanical Properties of Alloys near Composition TiNi", Journal of Applied Physics, volume 34, number 5, May 1963, pages 1475-1477.
3. Bueher, W.J.: "Intermetallic Compound Based Materials for Structural Applications", Proceedings of the 7th Navy Science Symposium: Solution to NAVY Problems Through Advanced Technology, May

14-16, 1963, U.S. Naval Aviation Medical Center, ensacola, Florida, voulme 1. Office of Naval Research, Arlington, VA, May 1963.

4. W.J. Buehler: "NITINOL Re-Examination", White Oak Laboratory Alumni Association Leaf, Winter 2006, volume VIII, Issue I, www.wolaa.org.

5. R.W. Roberts and R. S. Owens; Titanium Lubrication, Nature, volume 200, October 26, 1963, pages 357-358.

6. Jones, W.R.Jr., Pepper, S.V., Wheeler, D.R., Jansen, M.J., Nguyen, Q.N., and Schroer, A., "The Effect of Stress and TiC Coated Balls on the Lifetime of a Perfluoropolyalklether Using a Vacuum Rolling Contact Tribometer", Tribology Transactions, volume 43(2000), 4, 685-688.

7. M.N. Gardos, H.H. Hong, and W.O. Winer: "The Effect of Anion Vacancies on the Tribological Properties of Rutile (TiO2-x), Part II: Experimental Evidence", STLE Tribology Transactions, volume 33, number 2, April 1990, pp. 209-220.

8. M.D. McNeese, D.C. Lagoudas, and T.C. Pollock; "Processing of TiNi from Elemental Powders by Hot Isostatic Pressing", Materials Science and Engineering A280 (2000), pp. 334-348.

9. K. Otsuka and X. Ren: "Physical metallurgy of Ti-Ni-based shape memory alloys," Prog. Mater. Sci., vol. 50, pp. 511-678, 2005.

10. W.R. Jones, Jr., S.V. Pepper, M.J. Jansen, Q.N.Nguyen, E.P. Kingsbury, S. H. Loewenthal, and R. E. Predmore: "A New Apparatus to Evaluate Lubricants for Space Applications-The Spiral Orbit Tribometer (SOT), NASA TM-2000-209935.

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