Wear 496-497 (2022) 204309

Contents lists available at ScienceDirect

Wear

journal homepage: www.elsevier.com/locate/wear

Development of a new cryogenic tribotester and its application to the study of cryogenic wear of AISI 316 stainless steel

Francis E. Kennedy [a,*], Youxiong Ye [a], Ian Baker [a], Raina R. White [a], Robert L. Barry [a], Aubrey Y. Tang [a], Min Song [b]

[a] Thayer School of Engineering, Dartmouth College, Hanover, NH, 03755-8000, USA
[b] State Key Laboratory for Powder Metallurgy, Central South University, Changsha, 410083, PR China

ARTICLE INFO

Keywords:
Tribotesting
Cryogenic
Wear
Austenitic stainless steel

ABSTRACT

A pin-on-disk tribotester has been designed and constructed that enables cryogenic friction and wear testing to be conducted either in liquid nitrogen (wet tests) or in dry sliding conditions. The tester does not require a sealed, cooled cryostat for the cryogenic tests. For wet tests, both pin and disk specimens are immersed in liquid nitrogen (LN_2), whereas for the dry cryogenic tests, the disk specimen is only partially submerged in LN_2 while the pin specimen remains dry in gaseous nitrogen.

To prove the capabilities of the tribotester, tests were run using AISI 316 stainless steel pins in sliding contact with disks made of yttria-stabilized zirconia. Friction and wear tests were run under three conditions: dry sliding in room temperature air, cryogenic dry sliding in which bulk pin temperatures remained less than 115 K, and wet cryogenic tests in LN_2 at 77 K. All tests were run at two different sliding speeds, 0.1 and 1.0 m/s, for a sliding distance of 1 km. It was found that wear rates of the stainless steel material were slightly lower at cryogenic temperatures than at room temperature, with wear being greater at low sliding speed than at high speed for all test conditions. Friction coefficients in the cryogenic tests were generally slightly lower than those at room temperature. X-ray diffraction analysis of the worn AISI 316 stainless steel pin surfaces showed that phase transformation from austenite to martensite had occurred during all cryogenic wear tests, whether in liquid nitrogen or during dry sliding, as well as during tests in air at room temperature. More martensite was produced during low speed sliding tests, both wet and dry, when the wear rates were higher, than at high sliding speeds. X-ray photoelectron spectroscopy analysis of worn pin surfaces was conducted to determine the role of oxides in the wear process at both room and cryogenic temperatures.

1. Introduction

The friction and wear properties of materials at cryogenic temperatures (defined here as temperatures less than about 120 K [1]) became important in the mid-20th century with the development of rocket engines fueled by liquid oxygen (LOx) and liquid hydrogen (LH_2) for spacecraft and space exploration [2]. More recently, cryogenic temperatures have been encountered in a wide range of land-based applications, including pumps and other equipment for gas liquification, cryogenic refrigeration for material processing and food storage, superconducting magnets for medical resonance imaging and nuclear magnetic resonance, cryo-surgery, and many other uses. Because liquid lubricants cannot be used at such low temperatures, most contacting mechanical components such as seals, bearings, gears and pistons operating in cryogenic equipment necessarily encounter either dry sliding conditions or sliding contact in liquid cryogen, resulting in wear of the contacting surfaces. To evaluate the tribological performance of materials for use in those applications, cryogenic friction and wear test devices are required.

The first reported cryogenic tribotester was developed at the NACA/NASA Lewis Research Center in the 1950s [2]. It was used to study the friction and wear behavior of various polymers, solid lubricant coatings, metals and other materials that were being evaluated for use in bearings or seals for cryogenic space propulsion applications [2,3]. The pin-on-disk test device featured a pin or rider sliding on a rotating disk while submerged in liquid nitrogen (LN_2) at 77 K. Soon thereafter, several test devices were developed at the Institute for Low Temperature Physics and Engineering (ILTP&E) in Ukraine for testing the tribological

* Corresponding author.
E-mail address: francis.e.kennedy@dartmouth.edu (F.E. Kennedy).

https://doi.org/10.1016/j.wear.2022.204309
Received 3 December 2021; Received in revised form 6 February 2022; Accepted 1 March 2022
Available online 3 March 2022

properties of materials in cryogenic or space environments for potential application in the former USSR's space program [4]. Most of the devices were designed to test tribological properties of sliding materials in low temperature vacuum environments, which are not a focus of this current study. However, one of their cryogenic tribometers was a unique pin-on-disk tester inside a sealed metal cryostat that featured the capability of doing sliding tests in either a liquid cryogen (LN_2, LH_2, or liquid helium - LHe) or dry sliding tests in gaseous vapors of those cryogens at temperatures ranging from 4.2 K to 293 K. Tests were performed for polymers, solid lubricants and metals, including superconducting metals, and results are summarized in Ref. [4].

Subsequently, experimental studies were carried out in a number of laboratories around the world to evaluate cryogenic friction and wear behavior of various materials for other applications, including metallic materials in labyrinth seals for cryogenic fuel pumps [5], metals and polymers under fretting conditions in superconducting magnets [6], unfilled and solid lubricant filled polymeric materials for supports of cryogenic magnets [7], and friction and wear of metals during simulated cryogenic machining [8]. Most of those tests were carried out on task-specific tribotesters in which the materials of interest were tested in liquid cryogen, usually LN_2, and in configurations and test conditions that simulated actual components.

Problems of wear of rolling element bearings for turbomachinery operating at cryogenic temperatures have led to several studies of the wear of potential bearing materials. Slifka et al. [9] at National Institutes of Standards in Colorado designed and built a three ball-on-disk tribometer capable of running tests of rolling bearing materials in liquid oxygen at 88 K, as well as in flowing oxygen or inert gas at room temperature or at temperatures up to 1000 K. The device was used by Chaudhuri et al. to study the wear and surface damage of 440C stainless steel ball materials in LOx and in oxygen gas at room and elevated temperatures [10]. Naerheim [11] developed a unique multi-purpose tribometer in a sealed chamber that includes scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS) and Auger electron spectroscopy. The tribometer had the capability of running sliding or rolling tests in either pure vacuum or in a variety of gas atmospheres at temperatures as low as 78 K. However, very limited information was given about cryogenic tests that had been run with the device and no cryogenic wear test results appear to have been published. A high-speed cryogenic tribometer was designed and constructed in India by Subramonian and Basu [12] to test bearing balls of various materials in high-speed sliding or rolling contact at high contact stresses with a rotating disk in LN_2 or LHe environment. The group used their tribometer to test self-mated 440C and AISI 304 stainless steel in LN_2 at various sliding speeds [12], high-purity copper against hardened steel balls in LN_2 [13], and pure titanium against hardened bearing steel balls in LN_2 [14]. Sliding wear tests were performed in LN_2 for self-mated ceramic materials, including alumina, zirconia and silicon carbide; the results are summarized in Ref. [15].

Researchers at BAM in Berlin, Germany built several cryogenic ball- or pin-on-disk tribotesters in the 1990s [16]. One of the cryotribometers is of the bath cryostat type, with the sliding contact occurring in liquid cryogen (LN_2, LHe or LH_2), while two others are capable of running tests in either liquid cryogen (bath cryostat) or under dry sliding conditions in a gaseous environment of N_2, He or H_2 (flow cryostat). The three cryotribometers have been used in testing the low temperature friction and wear behavior of a variety of materials, ranging from diamond-like carbon coatings [16] to numerous austenitic stainless steel alloys [17–20] and solid lubricants [21] for a wide range of cryogenic applications. Some of the results of their studies of austenitic stainless steels will be discussed below.

It should be noted that all of the tribotesters mentioned above, including those few devices capable of performing dry cryogenic wear tests, were encased in sealed, insulated cryostats, making them rather sophisticated and expensive to construct and maintain.

Austenitic stainless steel alloys are currently the materials of choice for many cryogenic applications, such as superconducting magnets and their supports, magnetic resonance imagers, and defense uses including mine-hunter vessels and submarines. However, most austenitic stainless steel alloys can undergo a martensitic transformation when deformed at low temperatures [22,23] or when cyclically cooled to cryogenic temperatures [24]. Martensitic transformations have also been found to occur during sliding wear of austenitic stainless steels including AISI 316 at room temperature [25,26]. The resulting martensite makes the material susceptible to hydrogen embrittlement and renders the austenitic stainless steel ferromagnetic, potentially causing serious magnetic problems when used at cryogenic temperatures in superconducting magnet support structures, magnetic resonance imagers or other applications [24].

These phenomena have been investigated in several tribological studies carried out on austenitic stainless steel specimens during tribotests at cryogenic temperatures using one or more of the cryogenic ball-on-disk tribotesters at BAM in Germany. Hubner et al. [17,18] ran alumina balls against AISI 304 stainless steel disks in LN_2 (77 K) and LHe (4.2 K) and found more martensitic transformation at higher normal load. Pinto et al. [19] and Assmus et al. [20] investigated the effects of chemical composition and liquid cryogen on the martensitic transformation of austenitic FeCrNi alloys in tests in LN_2, LHe or LH_2. Each of the reported studies on the BAM tribotesters showed conclusively that martensitic transformation of the tested austenitic stainless steels occurred during cryogenic sliding in liquid cryogens, but none of the studies determined whether martensitic transformation of the alloys occurred during dry cryogenic sliding tests. In addition, the presence or absence of oxides on the worn surfaces of austenitic stainless steel tested at cryogenic temperatures was not mentioned.

More recently, Farrahi et al. [27] developed a more basic cryogenic tribometer in Iran and used it to study the wear of austenitic AISI 316 stainless steel in sliding contact with AISI 52100 steel in room temperature air and in LN_2. They found that the stainless steel exhibited lower wear when tested in liquid nitrogen at 77 K than when run dry in air at 293 K. The presence or absence of martensite in their worn specimens was not examined.

Another potential concern relative to magnetization of worn austenitic stainless steels is the occurrence of ferromagnetic or ferrimagnetic oxides, particularly Fe_3O_4, on the worn surfaces and in any wear debris. It is known that iron oxides, including Fe_3O_4, are found on the surfaces of AISI 316 stainless steel that was worn at room temperature [26], but no studies of the oxidation of the material during cryogenic wear tests have been reported up to now.

The objectives of the work reported in this paper were three-fold:

- Design and construct a relatively low cost pin-on-disk tribometer capable of running friction and wear experiments both in liquid nitrogen (wet sliding conditions) and in nitrogen gas at cryogenic temperatures (dry sliding conditions), as well as dry sliding in air at room temperature.
- Study the friction and wear behavior of AISI 316 austenitic stainless steel at room and cryogenic temperatures; ensure that the tested materials remain at cryogenic temperatures and the friction and wear results are consistent with reported data for similar materials.
- Determine whether martensitic transformation occurs in the AISI 316 material during sliding wear in wet and dry cryogenic conditions and whether ferromagnetic or ferrimagnetic oxides are produced on the worn surfaces.

2. Cryogenic tribometer design

The cryogenic tribometer was designed to study the basic tribological behavior of a variety of materials, and not to study any specific application or component geometry. For that reason, the most common tribometer model, stationary pin on rotating disk, or pin-on-disk, was selected. Before embarking on the design of the cryogenic pin-on-disk tribometer, a simplified thermal analysis was performed to determine what design parameters would be of most importance. It is known that whenever a pin slides on a disk, no matter what the initial temperature, there will be frictional heat generated at the sliding interface that could result in a considerable rise in temperature of the contacting pin and disk [28]. A major consideration in this design was the removal of frictional heat from the contacting components. This is not a major concern for tests conducted in wet sliding conditions, when the contacting components are continuously surrounded by fluid at 77 K to which all frictional heat can easily be transferred. It could, however, be a major limiting factor in dry cryogenic sliding tests. Preliminary analysis, using the methods developed in Ref. [28], showed that at least 95% of the frictional heat would enter the rotating disk, as long as that disk was cooled continuously during the test. Therefore, development of an effective cooling scheme for the rotating disk became the first design challenge. Using simplified heat conduction models, it was also determined that a means would need to be provided to transfer heat from the pin to liquid cryogen in order to keep the pin from heating up excessively during dry sliding tests. In addition, humid laboratory air would have to be kept away from the cold components of the tribometer to prevent the development of frost and ice that could interfere with the low temperature test conditions.

A schematic diagram of the cryogenic tribometer designed and built for this study is shown in Fig. 1. Many features of the new design are based on a room-temperature pin-on-disk tribometer that was built in our laboratory and has been used successfully in wear research for over 25 years [29]. This new device is enclosed in a sealed and insulated environmental chamber, into which dry nitrogen gas flows continuously to limit the amount of humid air in the chamber. A container of desiccant is placed within the chamber to help maintain the relative humidity in the chamber at or below 10% during a test to prevent the formation of frost or ice on the pin and disk specimens and on other components of the tribometer. The environmental chamber is in turn mounted in a negative pressure fume hood to evacuate excess nitrogen gas.

The test rig has a cylindrical disk specimen that is mounted on a large copper backing disk, which rotates in a liquid nitrogen basin for cryogenic tests, although the basin may be removed for dry sliding tests at room temperature (Fig. 2). The test disk specimen is mounted on the backing disk while the test basin is empty and the test rig is still at room temperature. The basin may be lowered away from the backing disk by means of a laboratory scissor jack (Fig. 1) to enable the backing disk to be removed and the test disk to be installed. The shaft on which the rotating disks are mounted is driven by a variable speed DC motor that is mounted above the environmental test chamber (Fig. 1). A timing belt/pulley combination connects the motor shaft to the disk drive shaft. The speed of the motor is set before a test at a value which will give the desired sliding speed at the wear track on the test disk. The rotational speed of the disk drive shaft is monitored continuously during a test to ascertain that the sliding speed remains constant. The copper backing disk has circumferential fins on its outer surface (Fig. 2) to enhance thermal convection to the surrounding LN_2 bath. The copper backing disk is always submerged in liquid nitrogen during a cryogenic test; this, along with the disk's large mass and high thermal conductivity, enables that disk to be held at approximately 77 K throughout a test. A filling tube supplies liquid nitrogen to the bath and is used to maintain the LN_2 level approximately constant during a test. The level of LN_2 in the bath depends on the test being run: For cryogenic dry sliding tests the LN_2 level is kept about 1 cm below the sliding surface of the test disk, whereas for tests in liquid nitrogen it covers the test disk and pin surfaces throughout a test. In either case, frictional heat that enters the test disk is transferred to liquid nitrogen from much of the test disk's outer circumference and is also conducted into the copper backing disk, from which it is transferred to LN_2 at 77 K.

Before a test, a fresh pin specimen is secured in the copper pin holder. The pin holder and pin are then lowered into a copper 'thermal' sleeve and secured tightly in place (Fig. 3). The thermal sleeve is attached to and surrounded by a phenolic casing with low thermal conductivity for insulation purposes. Cryogenic 'thermal grease' (Apiezon N) may be applied to the mating surfaces of the test pin and the copper sleeve during cryogenic dry sliding tests, in order to reduce thermal contact resistance between the pin and surrounding sleeve. A temperature sensor, composed of two silicon diodes, was used to monitor pin temperature during each cryogenic test. One of its diodes, the pin temperature sensor, is permanently attached to the thermal sleeve (Fig. 3), where its measuring nose is in close proximity to the pin at a location about 1 cm above the sliding surface. This enables continuous measurement of the 'bulk' or average temperature of the pin being tested. The other diode, the reference sensor, is located in the liquid nitrogen bath. The copper thermal sleeve is kept cold during the test by means of copper braid or strap that is suspended from the thermal sleeve into the liquid nitrogen basin (Figs. 2 and 3). (A similar copper strap was used for 'cold transfer' to pin specimens in the cryogenic tribometers developed at ILTP&E in Ukraine [4]).

The pin holder is supported on the end of a loading arm that is

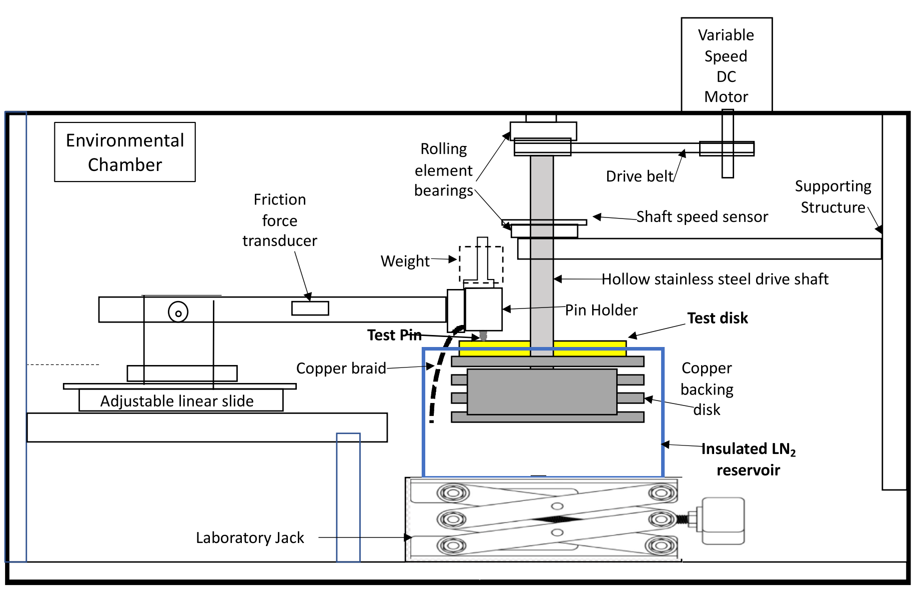


Fig. 1. Schematic diagram of cryogenic tribometer. (Not to scale).

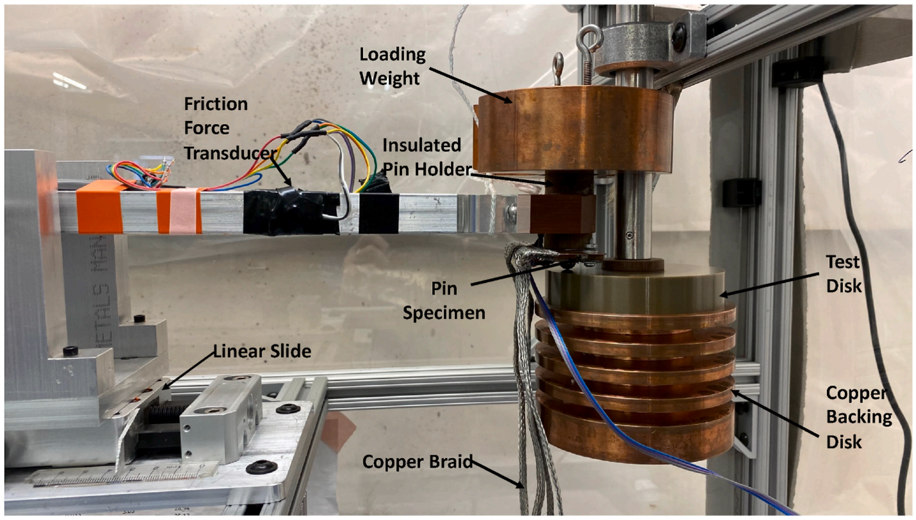


Fig. 2. Image showing rotating components of tribometer with liquid nitrogen basin removed.

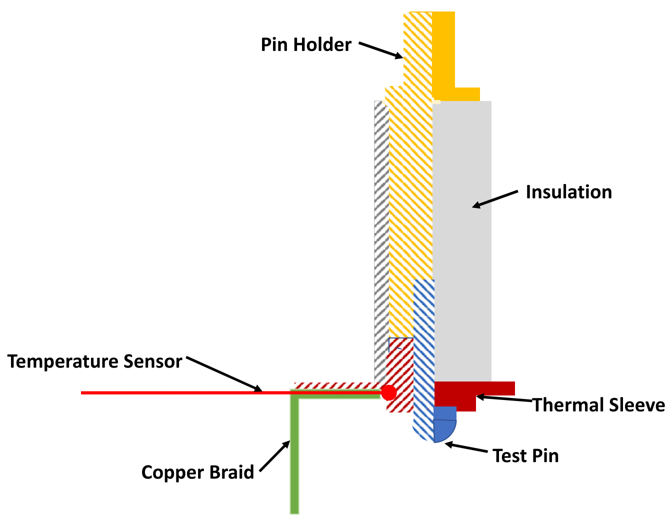


Fig. 3. Schematic diagram (cutaway) of pin holder assembly, including pin temperature sensor and copper braid for cooling pin.

instrumented with a strain gage-based friction force transducer (Fig. 2). That force transducer is identical to one that has been used on the earlier room temperature tribotester for over 25 years [29]. A 63.5 mm long central section of the aluminum loading arm was milled to create two parallel double cantilever beams separated by 50 mm. Each of beams has a height of 19 mm and a thickness of 1.25 mm, and each is instrumented with two horizontal strain gages, one on each face. This geometry provides high stiffness against bending moments caused by vertical forces and against torsion caused by twisting moments, but it has sufficiently low stiffness against bending moments caused by horizontal (friction) forces to produce measurable strains in the strain gages. The four identical temperature-compensated strain gages are connected in a Wheatstone-bridge arrangement, with output signal transmitted to a lab computer. The force transducer was calibrated by applying static horizontal forces to the pin in the friction force direction.

The location of the pin relative to the center of the rotating disk is set before a test by adjusting the linear slide on which the loading arm is mounted to set the predetermined radius of the wear track in an unworn section of the disk surface. The pin is loaded against the disk by a weight that is mounted directly above the pin. Both friction force and pin temperature are monitored continuously during a test and their values are stored on a computer, along with data from relative humidity measurements in the environmental chamber.

3. Experimental

3.1. Materials

A number of pin-on-disk tests were run to demonstrate the capabilities of the cryogenic tribometer and to resolve some discrepancies in the literature about the cryogenic wear behavior of austenitic stainless steel alloy AISI 316. That alloy is frequently used in cryogenic applications owing to its good mechanical properties and very good corrosion resistance over a wide temperature range, but there are concerns about whether martensitic transformation occurs in AISI 316 during cryogenic sliding and whether ferromagnetic or ferrimagnetic iron oxides are produced when the material is worn at cryogenic temperatures.

Pin specimens were machined from rods of commercially-produced hot-rolled and annealed 316 stainless steel. The pins had a diameter of 9 mm and had a hemispherical tip that had been polished to a surface roughness of <0.05 μm Ra. The pins were cleaned, dried and weighed before and after testing, and each pin was tested only once.

The counterface for the tribotests was a disk made from yttria-stabilized zirconia (YSZ). Because of the material's good mechanical properties and low thermal conductivity down to cryogenic temperatures, it has been suggested for use in cryogenic applications, such as a thermal shield for superconducting magnets [30]. In such applications, it is quite possible that it would encounter sliding contact with AISI 316 stainless steel, although no particular application was simulated in this test program. The zirconia disk for this study was 10 cm diameter and approximately 2 cm thick. It contained 2.8 mol.% yttria and was provided by Saint-Gobain Advanced Ceramics. The YSZ disk was polished to an average surface roughness (Ra) below 0.05 μm. Each test was run on an unworn track on the disk surface.

Prior to the series of tribotests, the hardnesses of the unworn pin and disk materials were measured using a TH713 Vickers hardness tester with 2.94 N load and 15 s loading time. Five indents were made on the ground and polished surfaces of samples with spacing of at least 2 mm between indents, and mean and standard deviation of the hardness values were determined for each material. The YSZ disk had a Vickers hardness value of 1339 ± 50 HV, whereas the hardness of unworn AISI 316 pins was 210 ± 17 HV.

3.2. Methods

Wear tests were performed at 0.1 m/s and 1.0 m/s sliding velocities in air at 295 K (room temperature dry sliding), in nitrogen gas at about 100 K (cryogenic dry sliding), and in liquid nitrogen at 77 K (cryogenic wet sliding). The normal load on the pins was 23 N in all cases and the sliding distance was 1 km for each test. The load and sliding velocities were selected to be consistent with recent room temperature wear tests of the same material combination [31], thus enabling comparison of friction and wear results for the two tribometers. Wear tests for each condition were repeated at least three times.

Prior to a test, after the test pin had been cleaned and weighed carefully, it was inserted in the pin holder. The pin was then set in contact with the disk surface at its predetermined location on the stationary disk surface, and the weight was set atop the pin holder. For cryogenic tests, the environmental chamber was then closed and dry nitrogen was supplied to the chamber. After the relative humidity in the chamber had reduced to an acceptable level (10% or less), LN_2 was supplied to the basin until the test disk and pin were submerged. As evaporation occurred, additional liquid was added until the pin temperature stabilized (approximately 77 K). For "wet tests", conducted with the pin submerged in LN_2, testing commenced immediately at the desired sliding speed and continued for a sliding distance of 1000 m. Liquid nitrogen was added to the test basin during the tests to ensure that the pin and disk surfaces remained covered with LN_2. For dry sliding tests, the liquid nitrogen level was allowed to drop to approximately 1 cm below the sliding surface before the test commenced. The LN_2 level was maintained at that level by adding more liquid nitrogen to the test basin when necessary.

Each of the worn pin specimens was cleaned after having returned to room temperature and its mass was again measured. The wear rate was determined by the change in pin mass during the 1 km sliding test. A Digital Precision scale lab analytical balance with 0.1 mg precision was used in all pin mass measurements. The worn surfaces of all pins were analyzed using a Thermo Scientific Helios 5CX Dual Beam scanning electron microscope (SEM) equipped with an Oxford Instruments UltimMax 100 energy dispersive X-ray spectrometer (EDX). Additionally, in order to examine the possible formation of martensite and ferrimagnetic iron oxides, X-ray diffraction (XRD) was performed on the worn pin surfaces using a Rigaku ultraX 18 diffractometer with Cu Kα radiation at a voltage/current of 40 kV/300 mA with step size of 0.02° at scanning rate of 1°/min. In order to determine the specific oxides present, X-ray photoelectron spectroscopy (XPS) measurements were performed on the worn pin surfaces using a spectrometer (ESCALAB 250; Thermo Fisher Scientific.

After several tests were run on a zirconia disk surface, the separate wear tracks were analyzed on an optical profilometer (ZYGO New View 7300, with MX 64 analysis software). Physical characteristics of each wear track were observed at several locations on the wear track, and the worn area of the groove cross-section beneath the original disk surface was calculated. The volumetric wear rate *Wv* for each track on the disk was determined by the following equation:

$$W_V = \pi \cdot D \cdot Aw \tag{1}$$

where *Aw* is the average worn area of the wear track on the disk and *D* is the mean diameter of the wear track. A disk surface was resurfaced after there was no more room for another wear track on the unworn surface.

4. Experimental results and discussion

4.1. Pin temperature during cryogenic sliding tests

A primary goal of the experimental tests was to ascertain whether the pin and disk temperatures remained within the cryogenic range (i.e., <120 K) during both dry and wet sliding tests. This was accomplished by continuously measuring the bulk temperature of the pins using the temperature sensor described above. Pin temperature measurements from typical wet and dry sliding tests are shown in Fig. 4.

As can be seen from Fig. 4, the bulk pin temperature was in all cases less than the goal of 120 K, so cryogenic temperatures were indeed achieved. This is not surprising for the 'wet' tests, in which the pin specimen was surrounded by liquid nitrogen, so the pin temperatures remained at or near the LN_2 boiling point of 77 K throughout a test. For the dry sliding tests the bulk pin temperature rose to nearly 100 K soon after the LN_2 level was lowered to about 1 cm beneath the sliding surface before a test began. Once sliding began, the bulk pin temperature rose further, but it generally remained less than 120 K, even for the high speed dry sliding cases. For all dry sliding test cases, the measured pin temperatures remained relatively constant in the range of 105–115 K. The results indicated that there was an increase of the bulk pin specimen temperatures during dry sliding as a result of frictional heating at the contact interface, particularly at high sliding speeds. However, the increase in bulk pin temperatures in the cryogenic tests was considerably less than what had occurred during dry sliding tests of the same materials at room temperature [31]. This is because most of the disk in the cryogenic tests remained at approximately 77 K owing to convective cooling of the outer diameter of the disk by the surrounding liquid nitrogen and most of the generated frictional heat was conducted into the cooled disk. The fact that bulk pin temperatures at the beginning of cryogenic dry sliding tests were higher than 77 K is due to the insufficient ability of the copper braid to transfer heat from the pin holder to the liquid nitrogen basin. A similar limitation evidently plagued the few cryostat-based tribotesters that have been constructed for cryogenic dry sliding tests [4,16]; that limitation caused the researchers to limit the loads on the test specimens or increase the 'cooling power' in order keep specimen temperatures within the cryogenic range. The only previously reported dry sliding tests at near cryogenic temperatures using a tribotester not enclosed in a cryostat were unable to maintain pin temperatures less than 150K [32].

4.2. Friction during cryogenic sliding tests

Before running any cryogenic tests, dry sliding tests of AISI 316 stainless steel pins against yttria-stabilized zirconia disks were run under the same load (23 N) and sliding speeds (0.1 and 1.0 m/s) in room temperature air. The mean steady-state friction coefficients for the room temperature tests were found to be approximately 0.6 at low sliding speed and slightly less (0.56) at higher sliding speed (Table 1). In comparison, friction coefficients for the same sliding materials and sliding conditions on the older room temperature sliding tester were measured to be 0.601 ± 0.098 at 0.1 m/s sliding speed and 0.552 ± 0.04 at 1.0 m/s [31]. Therefore, the friction measurements on the two test rigs were essentially the same, thus validating the friction force measuring capabilities of the new tribotester.

Friction was measured continuously during all cryogenic sliding tests, and typical plots of friction coefficient measured in wet and dry sliding tests at both low and high speeds are shown in Fig. 5. It is apparent that friction forces were variable during all sliding tests, but most noticeably during wet tests conducted at low sliding speeds. Based on these friction results, along with indications of increased vibration of the pin and pin holder components during low-speed tests, it was concluded that adhesion-related stick-slip type of contact was more prevalent at low sliding speeds than at high speed.

Most of the friction plots showed a running-in section that lasted for up to 200 m of sliding distance, with the friction coefficient during the running-in period usually starting at a lower value and increasing to a higher steady-state value. (The particular wet, high speed test result shown in Fig. 5 is a slight exception.) To determine the mean steady-state friction coefficient for each condition, the friction data for the final 800 m of sliding were analyzed and the results are shown in Fig. 6. Error bars on the bar graphs are determined by standard deviation of the

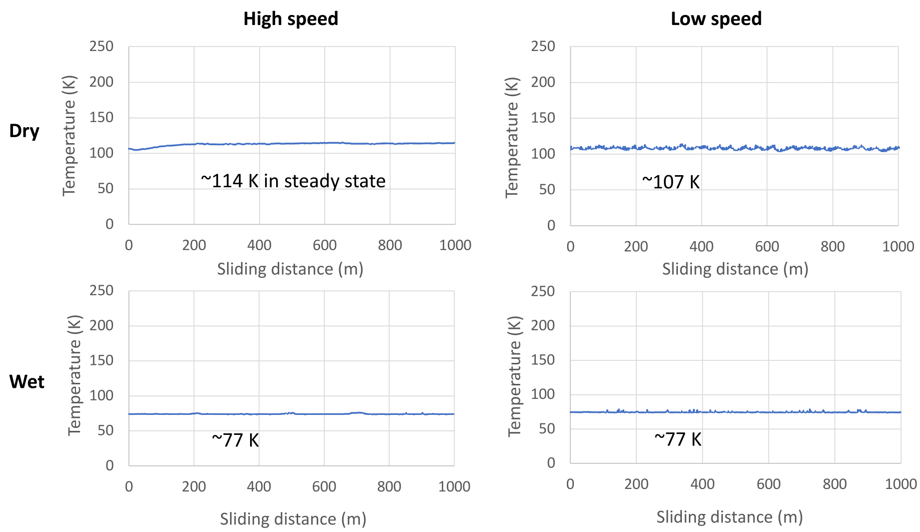


Fig. 4. Typical measured bulk temperatures of AISI 316 stainless steel pins during cryogenic sliding against yttria-stabilized disk.

Table 1
Measured friction coefficient and wear rate in room temperature tests
AISI 316 Stainless Steel pins in dry sliding in air against Yttria-Stabilized Zirconia disk. Normal load 23 N, Sliding Distance 1 km.

	1.0 m/s sliding speed	0.1 m/s sliding speed
Friction Coefficient		
Mean steady-state value	**0.56**	**0.60**
Standard Deviation	0.048	0.08
Wear Rate (mg/km)		
Mean value	**1.77**	**40.7**
Standard Deviation	0.48	15.7

friction coefficient data; the standard deviation is an indication of the variability of the friction for each case. In general, the mean friction coefficient was lower for the high speed cases, and the highest friction coefficient, as well as the greatest variability in friction, was found for the wet tests conducted at low sliding speed.

In summary, friction coefficients in the cryogenic tests were slightly lower than those at room temperature for similar test conditions, not considering the stick-slip conditions that occurred much more prominently in the cryogenic tests at low sliding speeds. Friction was less variable in the room temperature tests than in tests conducted at cryogenic temperatures, as indicated by the smaller standard deviations of the friction values at room temperature.

4.3. *Wear rates during cryogenic sliding tests*

Wear of the AISI 316 stainless steel pins measured during tests at room temperature showed a considerable influence of sliding speed on wear rate (see Table 1). In fact, wear at room temperature at 0.1 m/s was more than an order of magnitude greater than at 1 m/s, a finding that is consistent with a recent study in which the wear rate of 316 stainless steel against YSZ at room temperature on the earlier pin-on-disk tribotester was found to be 2.0 mg/km at 1.0 m/s and 53 mg/km at 0.1 m/s [31]. Therefore, the wear measurements on the two test rigs were essentially the same, thus providing further validation of capabilities of the new tribotester.

Wear rates of the stainless steel pin specimens for tests conducted at cryogenic temperatures are shown in Fig. 7. Wear was greater during tests run at low sliding speed (0.1 m/s) than at the higher speeds (1.0 m/s) for both wet and dry conditions. Wear rates at high speeds were essentially the same in both dry and wet cryogenic tests. However, there

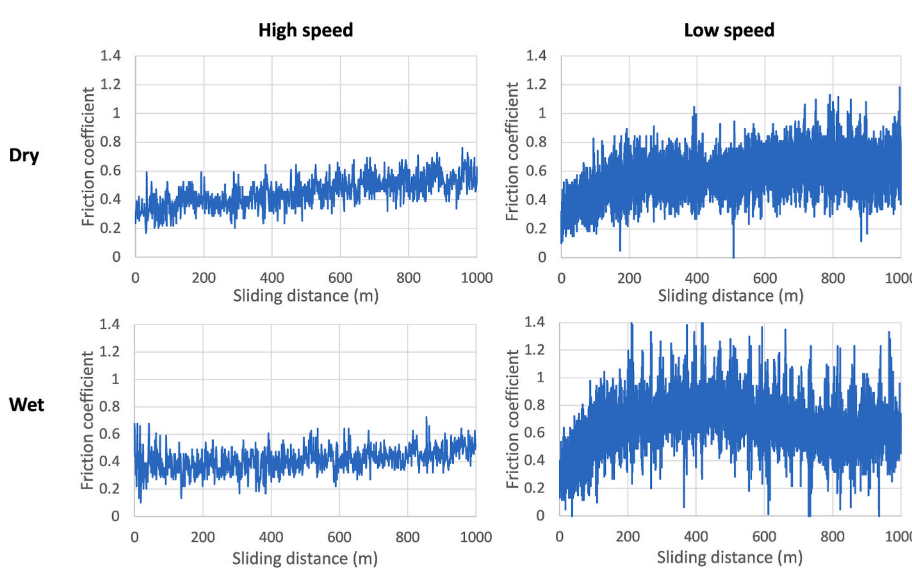


Fig. 5. Typical measured friction coefficient during cryogenic sliding of AISI 316 stainless steel pins against yttria-stabilized disk.

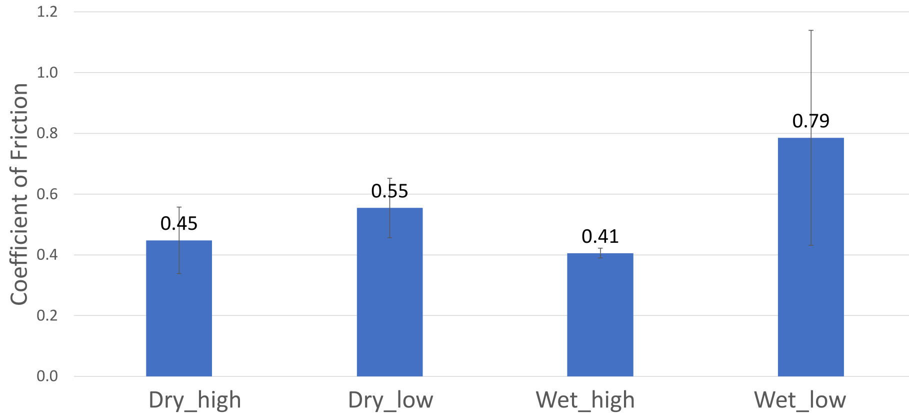


Fig. 6. Mean steady-state coefficient of friction during cryogenic wear tests of AISI 316 stainless steel pins against yttria-stabilized zirconia disk.

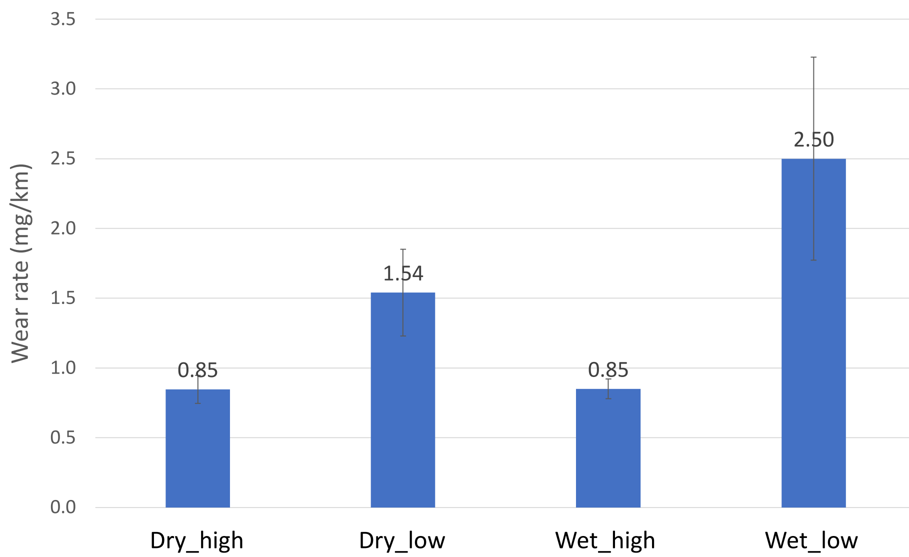


Fig. 7. Measured wear rates (mg/km) during cryogenic wear tests of AISI 316 stainless steel pins against yttria-stabilized zirconia disk.

was greater wear and more variability (greater standard deviation) in low speed tests run in liquid nitrogen than for dry low speed tests.

Optical profilometry of the wear tracks on the YSZ showed that mild wear of the zirconia had occurred during all tribotests. In an attempt to quantify the disk wear results, four wear tracks of tests run at different conditions on the same surface of a typical zirconia disk were examined and the total volumetric wear of the four tracks was calculated using Eq. (1). Results are shown in Table 2. In some cases, such as the dry, low speed wear track in Table 2, volumetric wear loss of the disk material could not be determined because of the presence of a substantial amount of transferred pin material on the wear track. In general, it can be seen that the worn volume of the zirconia disk was greatest in the liquid lubricated test conditions, indicating that more wear particles of zirconia may have been liberated in those cases.

Table 2
Volumetric wear of zirconia disk during cryogenic sliding wear tests
Volume loss (mm^3) in wear tracks on a Yttria-Stabilized Zirconia disk from tests against pins made from AISI 316 Stainless Steel pins in various cryogenic conditions. Normal load 23 N, Sliding Distance 1 km.

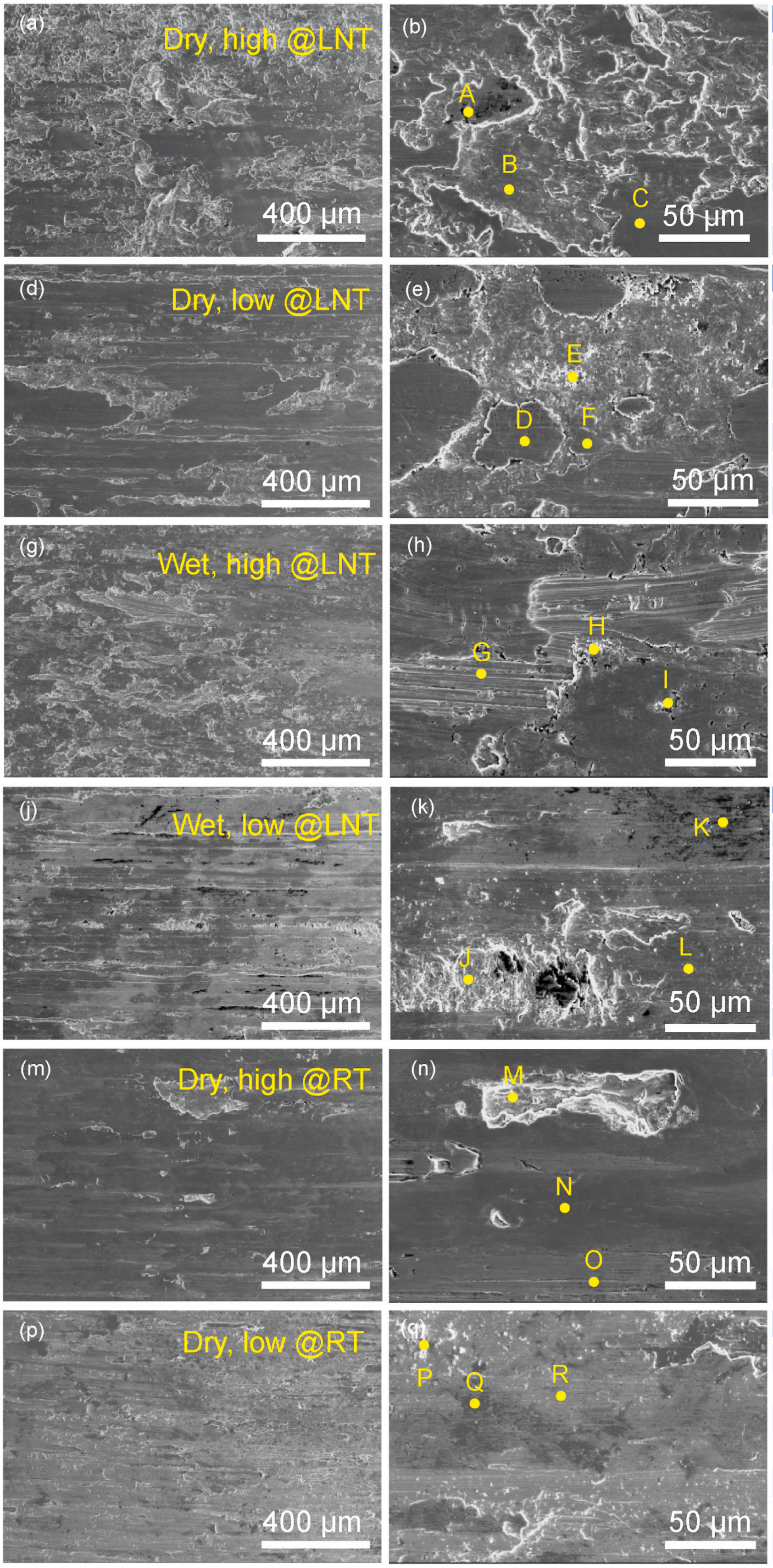
	1.0 m/s sliding speed	0.1 m/s sliding speed
Wet (in liquid nitrogen)	**11.3 x 10^{-3}**	**13.8 x 10^{-3}**
Dry (in dry nitrogen gas	**3.3 x 10^{-3}**	**

** indicates that volume loss of disk could not be measured because of transferred pin material on the wear track.

The results of the tribotests of AISI 316 stainless steel reported here have confirmed earlier conclusions [6,27] that wear of the material is slightly lower in liquid nitrogen than in room temperature air. Information presented here also shows that wear rates are not significantly different between cryogenic high-speed tests run dry and those run in liquid nitrogen. Cryogenic wear rates were lower at high sliding speeds than at low speeds in most cases. Further information about wear mechanisms of the 316 stainless steel alloy for the different test conditions was obtained by analysis of the worn surface.

4.4. Analysis of worn surfaces

Worn surfaces of all worn test pins were examined in an SEM equipped with EDX. Typical secondary electron images are shown in Fig. 8 for each test case. The worn stainless steel surfaces show considerable evidence of plastic deformation and smearing indicative of adhesive wear, particularly in the low speed tests that had shown the greatest wear (Fig. 8(d and e), 8 (j and k) and 8 (p and q)). There was also evidence of light abrasion, probably by third-body wear debris, on many of the surfaces. The surfaces that showed the least wear (all tests at high speed) appeared to be smoother than surfaces that had greater wear rates. The EDX results show that some locations on the worn surfaces (e.g., points F in Fig. 8(e), G in Fig. 8(h) and R in Fig. 8(q)) have essentially the same composition as the base AISI 316 stainless steel, which contains



(c)	A	B	C
O	60.7	23.8	/
Fe	19.0	50.9	78.0
Cr	6.8	13.7	2.4
Ni	2.1	7.1	18.2
Mn	0.6	1.0	/
Mo	/	1.0	1.3
Zr	10.6	1.5	/

(f)	D	E	F
O	33.8	48.8	5.7
Fe	43.1	32.1	61.5
Cr	12.0	9.3	17.7
Ni	6.1	4.6	9.4
Mn	1.1	0.9	1.8
Mo	/	/	1.5
Zr	1.8	2.8	/

(i)	G	H	I
O	6.9	62.2	36.9
Fe	62.2	22.8	41.1
Cr	17.6	6.6	11.5
Ni	8.8	3.0	5.6
Mn	1.5	/	1.1
Mo	1.2	/	/
Zr	/	2.2	1.9

(l)	J	K	L
O	52.9	47.8	13.9
Fe	29.9	33.6	56.9
Cr	8.5	9.6	16.3
Ni	4.0	4.8	8.3
Mn	0.7	0.8	1.4
Mo	/	0.7	1.3
Zr	2.6	1.9	/

(o)	M	N	O
O	51.8	62.0	22.0
Fe	31.4	25.1	51.3
Cr	9.2	8.4	15.1
Ni	4.7	1.9	8.0
Mn	1.0	0.8	1.4
Mo	0.7	0.5	1.1
Zr	0.6	1.0	/

(r)	P	Q	R
O	50.6	33.5	4.6
Fe	32.0	44.0	63.1
Cr	9.0	12.4	17.8
Ni	4.7	6.3	9.6
Mn	/	1.1	1.7
Mo	0.7	1.0	1.4
Zr	1.0	/	/

Fig. 8. Secondary electron images of worn surfaces of AISI 316 stainless steel pins after wear testing at various test conditions. Tabulated EDX output (At%) is given for selected points on the worn surfaces.

about 68 at% Fe and 17% Cr. On the other hand, other locations show that there has been some mechanical mixing in the worn surface layer, with composition that includes the base stainless steel as well as some zirconia from the counterface disk and some other oxides. It might be noted that the presence of oxygen on the worn surfaces for all test conditions indicates that oxidation had occurred, even in tests that were run submerged in LN_2 (more on that below).

To further investigate the changes in microstructure that occurred during wear of the AISI 316 stainless steel pins, X-ray diffractometry was used. In particular, it was of interest to determine whether or not phase change from austenite to martensite had occurred in the AISI 316 material during the wear process. Results of the XRD analyses are shown in Fig. 9. It is apparent from the XRD spectra in Fig. 9 that martensite had formed in the near-surface regions of all worn pin surfaces, whether the wear process had occurred at room temperature or at cryogenic temperatures, and whether the cryogenic tests had been run dry or in LN_2. These results agree with earlier studies that detected martensite formation during sliding wear of the austenitic stainless steels in dry sliding at room temperature [25,26] and cryogenic wear studies in liquid nitrogen [17,19,27]. This work has shown that martensite is also produced during dry sliding of 316 stainless steel at cryogenic temperatures, a result that has not been previously reported. These findings should be an important consideration for anyone designing magnetic resonance imagers or other equipment using superconducting magnets. Based on the strength of the martensite peaks relative to the austenite peaks, it appears that more martensite was produced during low speed sliding tests, both wet and dry, when the wear rates were higher, than at high sliding speeds.

It was also of interest to see whether any ferrimagnetic iron oxide (Fe_3O_4) was formed during the wear process. Although Fe_3O_4 was detected in the specimens that had been tested at room temperature (Fig. 9), no significant amounts of the magnetic iron oxide were found in the XRD spectra of surfaces that had been tested at cryogenic temperatures.

X-ray photoelectron spectroscopy (XPS) was utilized to determine with more accuracy the oxides produced during the wear process. Results of the XPS analysis are shown in Fig. 10. The amount of Fe_3O_4 for the room temperature (RT) conditions in the XPS data of Fig. 10(a) is consistent with the XRD results of Fig. 9, i.e., substantial amount of Fe_3O_4 after room-temperature, high-speed tests, but slightly less after room-temperature, low-speed tests. The XPS data also show detectable amounts of Fe_3O_4 on all worn surfaces, including the tests conducted in cryogenic conditions, particularly the low-speed test in liquid nitrogen (the test that had the highest wear rate). That finding wasn't picked up by the XRD results, probably because the XRD data come from a few millimeters depth beneath the surface, whereas the XPS data come from a depth of $<$10 nm. The XPS data in Fig. 10(b) show that Cr_2O_3 was present on the worn surfaces for all cases, and the data in Fig. 10(c) show that ZrO_2 was also present on all worn surfaces. Analysis of the data in Fig. 10(c) showed that there was more ZrO_2 on the surfaces worn at high speed than after the low-speed tests.

The EDX and XPS results in Figs. 8 and 10, respectively, demonstrate that there were significant amounts of oxides on the worn stainless steel pin surfaces. The origins of those oxides are worthy of discussion, particularly since the oxides were present after the wet tests, during which no oxygen is present.

Since there is no zirconium in the AISI 316 stainless steel pin material, the ZrO_2 found on all worn pin surfaces, see Fig. 10(c), must have been transferred from the zirconia disk during the wear process. Recent work [31] has shown that contact stresses and temperatures during sliding on yttria-stabilized zirconia can result in temperature- and stress-related transformation of the zirconia material in those conditions, resulting in pull-out of zirconia grains that can then transfer to the stainless steel pin surface. ZrO_2 is quite hard, with hardness of about 11 GPa [33]. Its presence on the wearing surface of the softer stainless steel pin serves to make the surfaces more resistant to wear. There was found to be more zirconia mixed into the wearing pin surface in high speed test cases, making the surface harder and more wear resistant; this is one likely reason that there was less pin wear in those cases than at lower speeds (Fig. 7). A similar conclusion was drawn in an earlier study of wear of various pin materials against zirconia at room temperature [31]. Another and probably even more important contributor to the greater wear in low speed test cases was the increased amount of adhesive interaction in those cases, as noted above.

It has long been known that very thin films of chromium oxide, and particularly Cr_2O_3, are present on all exposed surfaces of austenitic stainless steel [34]. That oxide film provides austenitic stainless steels, including AISI 316, with its well-known resistance to corrosion and

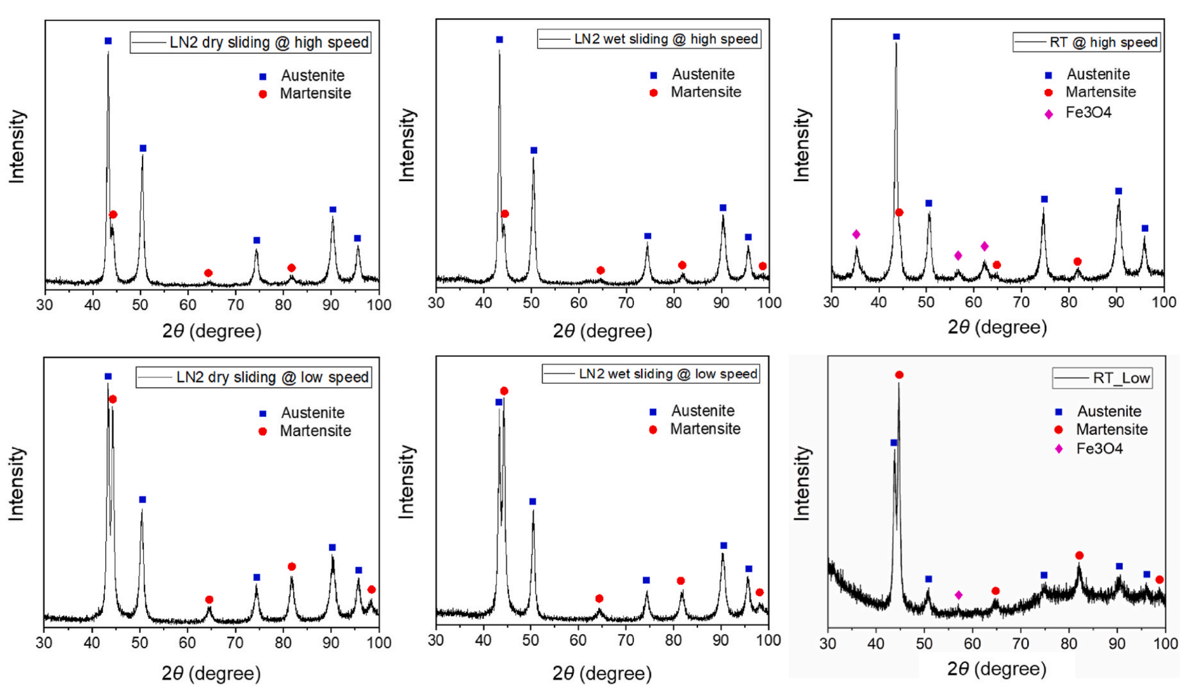


Fig. 9. X-ray diffractometry spectra from worn surfaces of 316 stainless steel test pin for different test conditions.

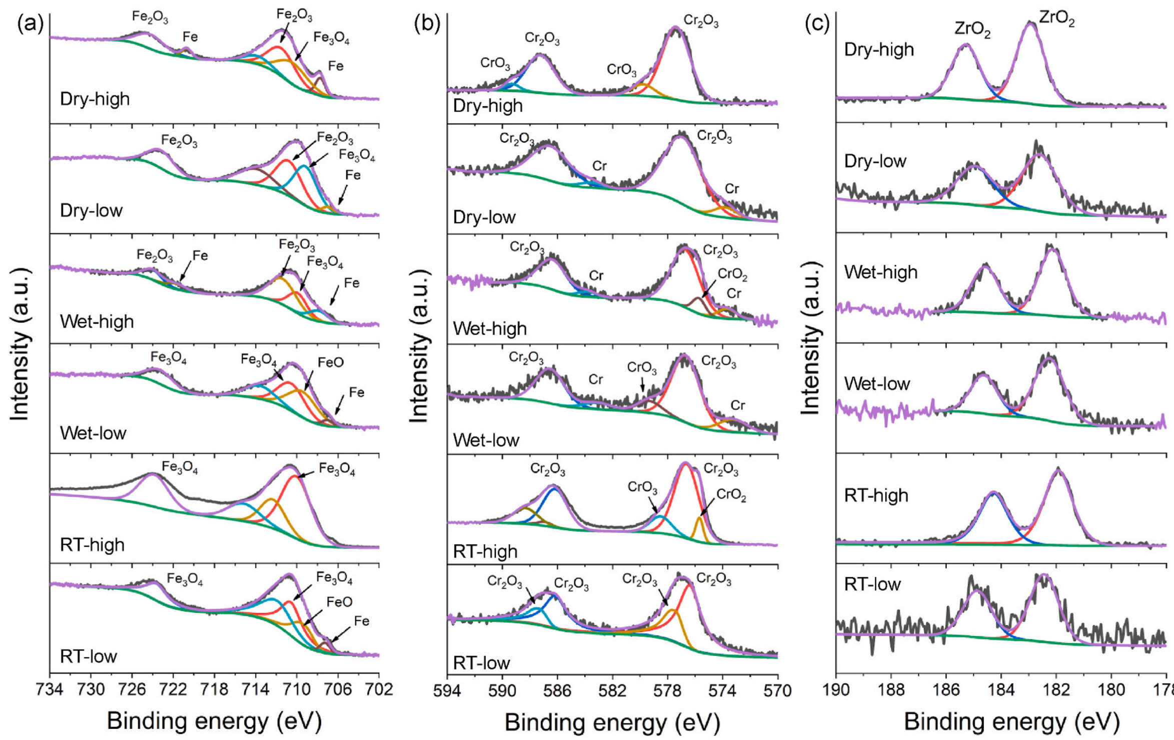


Fig. 10. X-ray photoelectron spectroscopy from the worn surface of AISI 316 stainless steel after wear tests against YSZ at various conditions; (a) Fe-2p spectra; (b) Cr-2p spectra; (c) Zr-3d spectra.

oxidation, making them 'stainless'. During the wear process, some of that thin protective film of Cr_2O_3 is removed and either expelled as wear debris or mixed into the near surface layer of deformed subsurface material. This is apparent from the SEM and EDX results in Fig. 8, although it is also apparent that some islands of Cr_2O_3 oxide film remain on the surface. The XPS results in Fig. 10(b) evidently pick up some of the original Cr_2O_3 film as well as some that had been mixed in with the surface layer of the worn pin material and some oxide that formed on the surface after the wear test. Cr_2O_3 is also quite hard, with hardness of about 29 GPa [33], so it also contributes to the wear resistance of AISI 316 stainless steel.

Iron (II,III) oxide (Fe_3O_4) was found on the worn surfaces after all tests. Although some of this oxide for the room temperature test cases likely occurred during the sliding test, in most cases, particularly those conducted in LN_2, the Fe_3O_4 is believed to be the result of oxidation of exposed iron on the worn surface the pin materials after the sliding tests. Recent work [35] has shown that oxidation of exposed iron in austenitic stainless steel occurs preferentially in room temperature air before oxidation of exposed chromium. Therefore, it is likely that most of the Fe_3O_4 found on the worn surfaces in the XRD and XPS results was produced in room temperature air during the period between the wear test and the surface analysis. The softer Fe_3O_4 (hardness of about 3 GPa) doesn't add much hardness to the surface, but it may limit adhesive interactions with the YSZ disk. However, Fe_3O_4 is ferrimagnetic and its presence on the worn surfaces and in wear debris could be detrimental in applications in which a strong magnetic field is present.

5. Summary

- A pin-on-disk tribotester has been designed and constructed that enables cryogenic friction and wear testing either in liquid nitrogen (wet tests) or in dry sliding conditions in nitrogen gas. The tester does not require a sealed, cooled cryostat for the cryogenic tests.
- During tribotests of AISI 316 stainless steel pins in sliding contact with zirconia disks, bulk pin temperatures remained at 77 K during wet cryogenic tests in LN_2 and remained less than 115 K during cryogenic tests in nitrogen gas.
- Wear rates of the stainless steel material were slightly lower at cryogenic temperatures than at room temperature, with wear being greater at low sliding speed than at high speed for all test conditions.
- Friction coefficients were lower for the high speed cases, and the highest friction coefficient, as well as the greatest variability in friction, was found for the wet tests conducted at low sliding speed.
- Friction coefficients in the cryogenic tests were generally slightly lower than those at room temperature.
- XRD analysis of the worn AISI 316 stainless steel pin surfaces showed that a phase transformation from austenite to martensite occurred during all cryogenic wear tests, whether in liquid nitrogen or during dry sliding, as well as during tests in air at room temperature.
- XPS analysis of the worn stainless steel surfaces revealed the presence of both hard, protective oxides, particularly ZrO_2 from the counterface zirconia disk, particularly in tests run at high sliding speed.
- Ferrimagnetic Fe_3O_4 was found on the worn surfaces; its presence could be detrimental in applications in which a strong magnetic field is present.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Ian Baker reports financial support was provided by US National Science Foundation.

Acknowledgements

This work was supported by U.S. National Science Foundation grant number 1758924. The authors wish to acknowledge the assistance of Christopher Levey, Michael Walsh and Jonah Sternthal for tribometer design, Lee Schuette and Dwayne Adams for fabrication, and Xiaobin

Guo and Jonathan Bonilla Toledo for wear testing.

References

[1] International Dictionary of Refrigeration, Int'l Inst. Of refrigeration (IIR). http://dictionary.iifiir.org/search.php, 2019.
[2] D.W. Wisander, W.F. Hady, R.L. Johnson, Friction studies of various materials in liquid nitrogen, NACA Technical Note 4211 (1958).
[3] D.W. Wisander, C.E. Maley, R.L. Johnson, Wear and friction of filled polytetrafluoroethylene compositions in liquid nitrogen, ASLE Trans 2 (1959) 58–66.
[4] Y.L. Ostrovskaya, T.P. Yukhno, G.D. Gamulya, Y.V. Vvedenskij, V.I. Kuleba, Low temperature tribology at the B. Verkin Institute for low temperature Physics and engineering (historical review), Trib. Int'l. 34 (2001) 265–276.
[5] F.X. Dolan, F.E. Kennedy, E.M. Schulson, An experimental investigation of rubbing interaction in labyrinth seals at cryogenic temperature, Wear 102 (1985) 51–66.
[6] A. Iwabuchi, T. Honda, J. Tani, Tribological properties at temperatures of 293, 77 and 4 K in fretting, Cryogenics 29 (1989) 124–131.
[7] P.C. Michael, E. Rabinowicz, Y. Iwasa, Friction and wear of polymetric materials at 293, 77 and 4.2 K, Cryogenics 31 (1991) 695–704.
[8] N.S.M. El-Tayeb, T.C. Yap, P.V. Brevern, Wear characteristics of titanium alloy Ti54 for cryogenic sliding applications, Trib. Int'l. 43 (2010) 2345–2354.
[9] A.J. Slifka, D.K. Chaudhuri, R. Compos, J.D. Siegworth, A tribometer for measurements in hostile environments, Wear 170 (1993) 39–44.
[10] D.K. Chaudhuri, A.J. Slifka, J.D. Siegworth, Friction and oxidative wear of 440C ball bearing steels under high load and extreme bulk temperatures, Wear 160 (1993) 37–50.
[11] Y. Naerheim, A SEM/AES/XPS tribometer for rolling and sliding contacts, Wear 162–164 (1993) 593–596.
[12] B. Subramonian, B. Basu, Development of a high-speed cryogenic tribometer: design concept and experimental results, Mater. Sci. Eng. A415 (2006) 72–79.
[13] B. Basu, B.B. Manoj-Kumar, P. Gilman, Sliding wear properties of high purity copper in cryogenic environment" J, Mater. Sci. 44 (2009) 2300–2309.
[14] B. Basu, J. Sarkar, R. Mishra, Understanding friction and wear mechanisms of high-purity titanium against steel in liquid nitrogen temperature, Metall. Mater. Trans. 40A (2009) 472–480.
[15] B. Basu, M. Kalin, Chaps. 27, 28 and 29 of Tribology of Ceramics and Composites: A Materials Science Perspective, John Wiley & Sons, 2011, ISBN 978-0-470-52263-9.
[16] T. Gradt, H. Borner, T. Schneider, Low temperature tribometers and the behaviour of ADLC coatings in cryogenic environment, Trib. Int'l 34 (2001) 225–230.
[17] W. Hubner, Phase transformations in austenitic stainless steels during low temperature tribological testing, Trib. Int'l 34 (2001) 231–236.
[18] W. Hubner, A. Pyzalla, K. Assmus, E. Wild, T. Wroblewski, Phase stability of AISI 304 stainless steel during sliding wear at extremely low temperatures, Wear 255 (2003) 476–480.
[19] H. Pinto, A.R. Pyzalla, W. Hubner, K. Assmus, Influence of environment, temperature and chemical composition on the microstructural deterioration of CrNi steels during friction, Mat. -wiss. U. Werkstofftech 35 (2004) 716–721.
[20] K. Assmus, W. Hubner, A. Pyzalla, H. Pinto, Structure transformations in CrNi steels under tribological stressing at low temperatures, Tribotest 12 (2006) 149–159.
[21] T. Gradt, T. Schneider, Tribological performance of MoS2 coatings in various environments, Lubricants 4 (2016) 32, https://doi.org/10.3390/lubricants40300032.
[22] T. Angel, formation of martensite in austenitic stainless steels, Journal of the Iron and Steel Institute (1954) 165–174.
[23] S.S. Hecker, M.G. Stout, K.P. Staudhammer, J.L. Smith, Effects of strain state and strain rate on deformation-Induced transformation in 304 stainless steel, Metall. Trans. A 13A (1982) 619–626.
[24] D.C. Larbalestier, H.W. King, Austenitic stainless steels at cryogenic temperatures – structural stability and magnetic properties, Cryogenics 13 (1973) 160–169.
[25] K.-L. Hsu, T.M. Ahn, D.A. Rigney, Friction, wear and microstructure of unlubricated austenitic stainless steels, Wear 60 (1980) 13–37.
[26] M.C.M. Farias, R.M. Souza, A. Sintora, D.K. Tanaka, The influence of applied load, sliding velocity and martensitic transformation on the unlubricated sliding wear of austenitic stainless steels, Wear 263 (2007) 773–781.
[27] G.H. Farrahi, V. Kazerani, M.S. Ghorashi, Test methodology and wear characteristics of austenitic stainless steel AISI type 316 at cryogenic environment, in: Proc. World Cong. On Eng'g. (WCE2014), vol. II, 2014, ISBN 978-988-19253-5-0.
[28] F.E. Kennedy, Y. Lu, I. Baker, Contact temperatures and their influence on wear during pin-on-disk tribotesting, Trib. Int'l 82 (2015) 534–542.
[29] B.J. Johnson, F.E. Kennedy, I. Baker, Dry sliding wear of NiAl, Wear 192 (1996) 241–247.
[30] S. Nishijima, A. Nakahira, K. Niihara, T. Okada, Applicability of ceramics for cryogenic use, Ceram. Trans. 43 (1994) 249–254.
[31] X. Guo, I. Baker, F.E. Kennedy, S.P. Ringer, H. Chen, W. Zhang, Y. Liu, M. Song, A comparison of the dry sliding wear of single-phase f.c.c. FeNiMnAlCr and CoCrFeMnNi high entropy alloys with 316 stainless steel, Mater. Char. 170 (2020) 110693.
[32] N.L. McCook, D.L. Burris, P.L. Dickrell, W.G. Sawyer, Cryogenic friction behavior of PTFE based solid lubricant composites, Tribol. Lett. 20 (2005) 109–113.
[33] J.F. Shackelford, W. Alexander, CRC Materials Science and Engineering Handbook, CRC Press, Boca Raton, FL, 2001.
[34] M.F. McGuire, Austenitic Stainless Steels", ASM International, Materials Park, OH, 2008, pp. 69–90 (Chapter 6) in Stainless Steels for Design Engineers.
[35] L. Ma, B. Lynch, F. Wiame, V. Maurice, P. Marcus, Nanoscale early oxidation mechanisms of model FeCrNi austenitic stainless steel surfaces at room temperature, Corrosion Sci. 190 (2021) 109653.