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Delivery Order 0068: Anti-fretting Coatings Research and Development

Carl Hager

Universal Technology Corporation

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14. ABSTRACT
This research in support of the Air Force Research Laboratory Materials and Manufacturing Directorate was conducted at Wright-Patterson AFB, Ohio from 14 November 2006 through 1 February 2008. This task worked to develop and test anti-fretting coating systems for application to Al and Ti alloys able to withstand high cyclic loadings in contact with steel counterparts. Fretting wear is an accumulation of damage that occurs at component interfaces that are subjected to high contact stresses coupled with low amplitude oscillation. In metallic contacts, surface oxides, adhesion, and material transfer play a primary role in the initial stages of fretting wear degradation. Given these behaviors, the focus of this study was to determine the effect of temperature on inter-metallic fretting wear between Ti6Al4V (Titanium, 6% Aluminum, 4% Vanadium) and cold-sprayed, commercially pure nickel coatings. The results presented herein show that increased temperature decreases friction through the formation of a uniform NiO layer, and by the reduction of Ni_2O_3 in the contact. In addition, it was found that a localized minimum friction coefficient is achieved at approximately 300ºC, above which the friction increases slightly due to the annealing of the cold sprayed coatings. *Alternate abstract on reverse*→

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14. **ABSTRACT (alternate)**

In metallic contacts, surface oxides, adhesion, and material transfer play a primary role in the initial stages of fretting wear degradation. Given this behavior, the focus of this study was to mitigate fretting wear within Ti6Al4V contacts at room temperature and 450°C with the use of thermally sprayed nickel graphite composite coatings with 5% to 20% graphite. The results show that the embedded graphite particles reduced the friction of the nickel thermal sprayed coatings during both low and high temperature fretting wear experiments. Friction and wear mechanisms are discussed with correlations of contact chemistry, morphology, and mechanical performance. Wear on the mated Ti6Al4V surfaces was reduced by the formation of uniform transfer films that were identified as graphitic based at room temperature and NiO based at 450°C.

1. Introduction

Fretting wear is a surface degradation phenomenon that typically occurs at component interfaces subjected to high contact stresses and low amplitude oscillations. In metallic contacts, surface oxides are often disrupted during the first few cycles. Once the surface oxides have been removed, the nascent metallic surfaces are exposed and strongly adhere to each other causing adhesive wear, or galling, to occur. Over time the active, or trapped, wear particles are broken up into finer debris and eventually oxidized [1].

In the aerospace industry, fretting wear of vibrating components made of low density high strength alloys is a critical problem that can lead to catastrophic failures. One of the most common occurrences of fretting in an aircraft turbine engine is in the compressor section at the blade/disk interface. The blade/disk interface, also known as the dovetail joint, is typically fabricated from Ti6Al4V alloy because of its high strength to weight ratio and corrosion resistance. Tribologically, mating Ti6Al4V surfaces are especially susceptible to fretting because titanium alloys have a propensity to gall. This can produce oxide debris, with higher hardness than the base alloy, that score the interface [2-4]. In addition to fretting wear at the interface, the combination of the rotating disk and the airflow through the engine imposes centrifugal forces and circumferential oscillations on the blades. This causes low amplitude cyclic stresses in the bulk material. The combination of the bulk cyclic stresses and fretting surface interactions promotes surface crack initiation and growth, which is often called fretting fatigue [5-7].

The impact of fretting wear on the reduction of fatigue life has been addressed in many publications. In 1995, Zhou et al. conducted a study using aluminum alloys that showed that fretting wear can cause surface tears or cracks that are long enough to be considered critical without bulk loading to the specimen [8]. In this work the authors conducted fretting wear tests using a spherical rider loaded normally onto a flat plate. Tests were conducted under various stroke lengths (~20-70 μm) and loads (~100-1200 N) for increased test durations. At the completion of each test, the samples were cross-sectioned and the fretting wear tracks were investigated for cracks. Zhou et al. found that during their tests, without bulk loading of any kind, cracks were formed in the fretting contact. It was also found that cracks (greater than 50 μm) can be formed very quickly when the tests were conducted in the mixed fretting regime. The observance of this cracking phenomenon under pure fretting wear conditions (without bulk loading) was also confirmed within Ti6Al4V contacts in 2004 by Swalla et al [9]. In 2005, Hutson et al. conducted extensive fretting fatigue crack analysis of Ti6Al4V contacts, and established that cracks greater than 50 μm can produce a dramatic reduction in fatigue strength [10].

One common mitigation strategy to the fretting wear/fatigue problem in titanium alloy compressor blades is to apply plasma sprayed CuNiIn (Copper-Nickel-Indium) or Al-bronze (aluminum bronze) plasma sprayed coatings and solid lubricants to the dovetails of the Ti6Al4V compressor blades, as shown in Fig 1 [11,12]. In some cases a solid lubricant is also applied to the disk slot; however, the slot geometries are often too small for the application of a plasma sprayed coating. Therefore, the CuNiIn or Al-bronze coating and solid lubricant, applied to the blade dovetail, were designed to act as a sacrificial barrier that protects both the blade and disk by preventing the Ti6Al4V surfaces from coming in contact with each other.

The roughness of the soft plasma sprayed metallic coatings is used as a retainer for the application of the bonded solid lubricant. The implementation of this strategy has increased component life; however, recent studies have shown that unlubricated CuNiIn and aluminum bronze coatings can cause severe damage to mating Ti-alloy counterparts [11,13]. In 2000, Freimanis et al conducted a fretting wear analysis of Ti-alloy blades and their mated disks after engine operation [11]. They found that the solid lubricant had worn away and the CuNiIn coated dovetails had caused significant damage to the uncoated disk. Fig 2 shows an example of the transfer of titanium to the surface of a CuNiIn coated blade dovetail, via galling with the uncoated disk. This clearly shows that the CuNiIn coatings can have a detrimental impact on the fretting fatigue life of uncoated titanium alloy disks (via galling at the interface) once the applied lubricants wear out.

This paper reports the development and investigation of a new mitigation strategy. This new strategy is based on the high temperature potential of nickel coatings to produce lubricious oxides and the low temperature use of graphitic solid lubrication to prevent galling at the metallic interface over a broad temperature range. The use of a commercially pure Ni thermal sprayed coating was chosen based on the literature which suggests that nickel alloy contacts perform very well in fretting wear contacts at elevated temperatures (in excess of 800°C) due to the formation of what is often called a 'Glaze' oxide layer [14-21]. It is believed that this is a similar phenomenon to that which Freimanis et al described in their fretting wear experiments with cobalt coatings, which the authors recommended for fretting wear mitigation at temperatures in excess of 450°C [22]. This potential for good fretting wear protection at elevated temperatures is appealing, because Ti-alloy compressor blades can be used at temperatures as hot as 450°C.

Graphite based solid lubricants are often bound using a silicate and applied to the surface of the plasma sprayed CuNiIn or Al-bronze coatings. In this work, the graphite was imbedded within the thermal sprayed nickel coatings to create a self lubricating composite surface on the Ti6Al4V surfaces. This composite would then negate the need for a bonded solid lubricant on the surface of the coating.

All of the fretting wear experiments were conducted under gross slip fretting wear conditions. It has been previously reported that the resultant wear is strongly affected by a mixture of gross slip and mixed fretting wear conditions [11]. In fact, Freimanis et al. were not able to mimic the fretting wear conditions of the engine without a two phase fretting wear test that combined an initial phase of gross slip fretting, followed by a primary phase of mixed fretting [11]. They believed that this was due to the fact that the blades experience a significant amount of gross slip fretting wear during the startup and shutdown of the engine. Because gross slip fretting wear is defined by a higher wear rate than mixed fretting, as shown in Fig 3, the authors of this work believe that it is pertinent to understand and mitigate the wear mechanisms associated with this phase of the coating degradation. In addition, special attention was paid to the degradation of both wear surfaces, which were investigated with a number of surface analytical techniques to reveal surface tribo-chemical adaptive mechanisms of the novel nickel graphite composite coatings.

2. Experimental

2.1 Specimens

The specimens used for this investigation were Ti6Al4V, and the test geometry was an ellipsoid on a flat plate. The ellipsoid, shown in Fig 4, was designed to eliminate the stress concentrations that occur at the edges of cylindrical contacts. Therefore, the Hertzian contact stress profiles for the samples are smooth with a maximum stress at the center instead of near the edge of contact. In addition, the elliptical contact simplifies alignment procedures for reproducible contact areas, and the large radius in the sliding direction allows for a target maximum Hertzian contact pressure of 650 MPa with an applied normal load of 50 N [24]. The plates were flat circular disks with a diameter of 12.7 mm on the test face and 3.2 mm thick. Average surface roughness (Ra) was 0.1μm on both the disk and the ellipsoid. Prior to testing, the Ti6Al4V disks were commercially grit blasted and then thermal sprayed with Ni based coatings. For proof of concept, nickel graphite abradable coatings were also applied to a few Ti6Al4V substrates. Abradable coatings are designed for low friction and high wear, therefore they are flame sprayed porously and have approximately 50% graphite powder in the pre-spray mixture. In addition to the abradable nickel graphite (NiG-A) coatings and the commercially pure thermal sprayed Ni coatings, a set of coatings were made using thermal spray with approximately 5%, 10%, and 20% (by volume) of graphite powder in the pre-spray coating mixture. These coatings were made to determine the graphite concentration required to get lower friction and lower wear rate compared the NiG-A coatings.

The flat disks and thermal sprayed Ni based coatings were used to simulate the surface of the blade dovetail, and the uncoated Ti6Al4V ellipsoids were used to simulated the surface of the slotted disk the in bench level fretting wear experiments. The properties of the Ti6Al4V substrates and the commercially pure thermal sprayed Ni coatings are listed in Table 1.

2.2 Tribological Testing and Analysis

The purpose of this work was to provide an understanding of how Ti6Al4V performed when coupled with nickel graphite composite thermal spray coatings, when subjected to gross slip fretting wear at room temperature and 450°C. The room temperature tests were conducted to simulate cold engine startup, and the 450°C experiments were conducted to mimic the highest temperature that Ti6Al4V might be subjected to within an aircraft engine. Three to four repeat tests were conducted on each coating. The tests were conducted using a 200 μm stroke length, 30 Hz oscillation speed, and a 50 N normal load for 100,000 cycles. In addition, shorter duration tests were conducted at 2 Hz oscillation speed, to supplement the longer tests for interfacial wear analysis.

For the duration of each test, the root mean square (RMS) of the friction data and the frictional hysteresis were recorded. The fretting wear tribometer, illustrated in Fig 5, has a stage that is mounted on thin metal legs that can support the normal applied load, while acting as tangential springs in the oscillation direction. As the elliptical sample moves the friction force between the samples causes the sample stage to deflect slightly, on the order of 1 μm typically, in the direction of sliding. The stage deflection then compresses or stretches the attached piezoelectric transducer and creates a signal. The signal from the piezo is then amplified and calibrated, using a force meter, to match the amount of force applied to the stage prior to testing. The friction force is then collected using an oscilloscope data acquisition card and a computer. Once collected, the RMS of the friction force is tabulated and plotted per test cycle in situ. In addition, a laser measuring system, depicted in Fig 5, is focused on the face of the oscillating arm of the tribometer and is used to continuously track the displacement of the ellipsoid during each test. The real time displacement data along with friction data and are then collected using the same oscilloscope computer card and are plotted to produce in situ hysteresis loops that provide real time monitoring of the fretting wear regime.

There have been a number of papers published that explain the use of hysteresis loops for the determination of fretting wear regime [24-30]. Elliptical shaped hysteresis loops have been shown to depict mixed fretting behavior and quasi-rectangular shaped hysteresis loops have been shown to depict gross slip behavior. This technique was used to ensure that each test operated in the gross slip regime throughout the entire duration of the test.

Once the fretting wear tests were completed, post test analysis was performed using scanning electron microscopy (SEM) and 3-D contact profilometery for morphology, along with energy dispersive spectroscopy (EDS), x-ray photoelectron spectroscopy (XPS), and Raman spectroscopy for chemical analysis.

3. Results

3.1 Friction Comparison

Fretting wear experiments were initially conducted on the commercially pure Ni coatings. The coefficients of friction for the Ni mated with Ti6Al4V fretting wear experiments were approximately 0.8 and 0.55 at room temperature and 450°C respectively. The NiG-A coatings yielded coefficients of friction that were approximately 0.25 and 0.35 at room temperature and 450°C respectively, when mated with the Ti6Al4V ellipsoids. However, the high graphite content and high porosity of the NiG-A coatings caused an increase in wear of more that six times that of the commercially pure Ni coatings (at both room temperature and 450°C). Therefore experiments were conducted on nickel graphite thermally sprayed composite coatings with initial volumetric powder loadings of 5% (NiG-5), 10% (NiG-10), and 20% (NiG-20) graphite. Fig 6 shows the measured coefficients of friction from each of the nickel graphite composite coating mixtures tested at room temperature. The lowest coefficient of friction (at just under 0.35) was exhibited between 5% and 20% graphite content in the pre-spray mixture. Therefore, the 10% graphite pre-spray mixture was considered to be the best choice for further experimentation.

Further experimentation was conducted on the selected NiG-10 coatings at 450°C. The friction and wear results from these experiments, in comparison to the results from the room temperature and 450°C tests on the NiG-A coatings and the commercially pure Ni coatings, are plotted in both Fig 7 and Fig 8 respectively. Although the measured coefficient of friction in the NiG-10 experiments were 0.1 and 0.05 higher than the values exhibited by the NiG-A coatings at room temperature and 450°C respectively, the NiG-10 coating wear was one sixth that of the NiG-A coating wear at room temperature and an order of magnitude lower at 450°C.

3.2 Wear Analysis

Initially, adhesive wear is the primary wear mechanisms that cause interfacial damage in Ti6Al4V and Ni coated interfaces during unlubricated gross slip fretting wear. During this period of initial wear, titanium from the ellipsoid surface and nickel from the coating surface is transferred to the opposing surface. Fig 10 shows the scanning electron microscope (SEM) images of typical nickel coating wear tracks after just 10 and 100 cycles of gross slip fretting against a Ti6Al4V ellipsoid. After 10 fretting wear cycles, some of the transferred fragments of titanium can be as large as 50 µm in size. However, these adhered titanium particles can grow to be as large as 200 µm in size after 100 cycles of unlubricated wear. Fig 10 shows a side by side comparison of the wear on the Ti6Al4V ellipsoid and the wear on the Ni coating after 100 cycles. This figure again shows the titanium adhered to the Ni coating, but it also shows the exact regions of the counterface where the titanium was removed. The white regions in Fig 10B are Ni that has transferred to the ellipsoid.

After approximately 1,000 cycles of gross slip fretting, debris accumulation in the contact caused the primary wear mechanism to transition from an adhesive type to a 3rd body type wear. Fig 11 and Fig 12 show a chronology of the wear tracks on the Ni coating and Ti6Al4V ellipsoid surfaces (respectively) after 10, 100, and 1,000 cycles of fretting wear. After 100 cycles, the adhered metallic material on both surfaces becomes so severely deformed that it breaks up into debris. Because of the nature of fretting wear, the majority of these wear debris are trapped within the interface and gets broken down into smaller and smaller particles. Most of these particles eventually oxidize and continue to damage both the Ni coating and the Ti6Al4V surfaces.

In order to combat the aforementioned wear mechanisms that were identified in the fretting wear of Ti6Al4V and Ni coated surfaces, the adhesive wear between the surfaces must be eliminated. One mitigation strategy, investigated herein, was to make a self-lubricating composite coating with a nickel matrix. For proof of concept, NiG-A composite coatings were tested under the same fretting wear conditions against Ti6Al4V. Fig 13 shows the chronology of the wear on the Ti6Al4V mated surfaces after 10, 100, 1,000, and 10,000 fretting wear cycles against the NiG-A coatings. The low friction exhibited by these coatings is guided by the formation of a transfer film that gradually smears onto the mated Ti6Al4V surface. Unlike the commercially pure Ni coating wear tracks, the NiG-A coatings did not cause any galling at the interface and induced very minimal damage to the Ti6Al4V ellipsoid surface. Even after 100,000 cycles of wear, shown in Fig 14, the ellipsoid still exhibited a stable lubricious transfer film. The surface of the NiG-A coating was also smooth and there wasn't any evidence of 3rd body wear.

The NiG-A coating successfully ameliorated the gross slip fretting wear during the room temperature experiments, but the wear rate of the coatings was not acceptable. Therefore, the 10% pre-spray mixture NiG-10 coatings were tested under the same room temperature fretting wear conditions. Fig 15 shows the chronology of the NiG-10 wear on the Ti6Al4V ellipsoid surface. Although there was some moderate adhesive wear damage during the first 10 cycles, these worn regions were quickly filled in by the formation of a lubricious transfer film (similar to that seen in the NiG-A wear tracks). This transfer film continued to expand its coverage of the interface throughout the duration of the fretting wear experiments. The formation of this film protected the Ti6Al4V ellipsoids from further wear. After 100,000 cycles, the transfer film virtually covered the entire contact region, Fig 16. In addition, the NiG-10 wear track was still smooth without any evidence of 3rd body debris accumulation or wear.

At room temperature the added graphite in the NiG-10 coatings reduced the coefficient of friction from 0.8, with commercially pure Ni coatings, down to just under 0.35. At 450°C, the addition of graphite in the composite NiG-10 coatings reduced the friction from just above 0.5, with commercially pure Ni coatings, down to approximately 0.45. This difference appears modest; however, the reduction in wear on the Ti6Al4V interface was very significant. Fig 17 shows the chronology of the wear on a Ti6Al4V ellipsoid that was worn against a NiG-10 coating at 450°C. The wear was very similar to what was exhibited at room temperature, but there was even less damage to the Ti6Al4V surface during the first 10 cycles of fretting. There was also a significant transfer film after just 10 wear cycles. This took approximately 100 cycles to form on the Ti6Al4V ellipsoid surfaces during the room temperature tests. Fig 18 shows the wear tracks on both the Ti6Al4V and NiG-10 surfaces after 100,000 cycles of wear. Even after 100,000 cycles of fretting there was still a stable transfer film on the Ti6Al4V ellipsoid, and the NiG-10 wear track was smooth and uniformly worn. For comparison to the baseline, Fig 19 shows the same chronology of wear on a Ti6Al4V ellipsoid mated with a commercially pure Ni coating at 450°C. After 10 cycles of wear, the Ni coating caused significant adhesive wear on the Ti6Al4V surface. In addition, fragments of the Ni coating were adhered to the ellipsoid wear track. As the wear progressed, more and more nickel transferred to the Ti6Al4V ellipsoid. The creation of this transfer film reduced the further degradation of the Ti6Al4V surface. However, the transfer film created by the Ni coatings was not as stable as the film formed by the NiG-10 coatings. This was due to the formation of debris within the wear track that caused some 3rd body wear. These active 3rd bodies may have been disruptive during the transfer film formation, and prevented it from forming a uniform layer, as seen in the wear tracks mated with the NiG-10 coatings.

3.3 Surface Chemistry

XPS for nickel-oxygen compositions have been well characterized in the literature [31-33]. Using XPS for surface analysis, Kim et al found that there is always some Ni_2O_3 present in the surface oxide at temperatures below 250°C in air, with an increased ratio of NiO to Ni_2O_3 with increased temperature [32]. The ratio increases because Ni_2O_3 is reduced thermally to NiO, since NiO is thermodynamically favored at higher temperatures.

At the conclusion of the fretting wear experiments, x-ray photoelectron spectroscopy (XPS) of the worn NiG-10 coatings and Ti6Al4V ellipsoids was performed to determine the effect that the combination of fretting and increased bulk temperature had on the surface chemistry in the wear track. Fig 20 shows the survey scans taken in the wear tracks of the mated surfaces. The most noticeable difference between the room temperature and 450°C worn surfaces was the fact that there were more intense Ni 2p peaks (labeled as nickel) in spectra from the 450°C wear tracks. The high resolution XPS scans of the NiG-10 coating wear track are shown in Fig 21. The Ni 2p peaks show definitively that the NiG-10 coating surface, worn at 450°C, contained predominantly NiO within the wear track. However, the slight evidence of nickel oxide present in the room temperature experiments suggested a higher oxidative state (the presence of Ni_2O_3). When Ni_2O_3 is present, the Ni $2p_{3/2}$ peak at ~ 855.5 eV becomes more intense relative to the Ni $2p_{3/2}$ peak at ~ 854 eV (both peaks are marked with dotted lines in Fig 21A). This shift in relative Ni $2p_{3/2}$ peak intensity is followed by an increase in intensity of an O 1s peak at ~ 531.7 eV. This change is shown in Fig 21B. NiO yields a spectrum with a more intense O 1s peak at ~ 529.5 eV. In addition, Fig 21C shows the high resolution scans of the carbon C 1s peaks to shown that there was not a bulk shift in the entire scan across all eV values.

High resolution scans of the Ti6Al4V ellipsoid wear tracks, shown in Fig 22, were taken in order to more accurately define the transfer film within the wear track after the room temperature and 450°C experiments. This analysis shows that the transfer films on the Ti6Al4V surfaces after the room temperature experiments were defined as containing carbon, TiO_2, and trace amounts of Ni_2O_3. The transfer films on the worn Ti6Al4V surfaces tested at 450°C contained mostly NiO and carbon, with trace amounts of TiO_2. The nickel oxide states are defined by the Ni 2p and O 1s peaks shown in Fig 22A and Fig 22B respectively. These peaks are almost identical to the peaks that were identified in the NiG-10 coating wear tracks after tests at the same respective temperatures. The presence of TiO_2 is defined by the shift of the Ti 2p peaks to ~ 458.8 eV, as shown in Fig 22C.

In the literature there is mention of a binary or double oxide that may form with the mixture of titanium and nickel oxides at high temperatures [34-37]. This complex oxide is not well characterized and is defined as $NiTiO_3$ or nickel titanate. However, one XPS study of this complex oxide suggested that it has a Ni^{2+} peak at (854.8 eV) and a Ti^{3+} peak at (457 eV) [37]. The 854.8 eV peak would be located between the Ni $2p_{3/2}$ peaks that describe NiO and Ni_2O_3, and is not apparent in the spectra shown in Fig 21A and Fig 22A. In addition, the Ti $2p_{3/2}$ peak at 457 eV is clearly not present in any of the spectra from the Ti6Al4V surfaces, as shown in Fig 22C. Therefore, there is no current evidence of the formation of this complex oxide in the XPS data obtained in this study.

In addition to XPS, a Raman microscope with a 514 nm wavelength laser was also used to analyze the NiG-10 and Ti6Al4V wear tracks, and better define the state of carbon within the wear tracks. Fig 23 shows the Raman spectra collected from the smooth lubricious regions in the NiG-10 coating wear tracks, as well as spectra from the transfer films on the Ti6Al4V ellipsoids. The analysis showed that a graphitic film did form in the NiG-10 and mated Ti6Al4V wear tracks, during the room temperature experiments. This helped to confirm that graphite particles within the composite did in fact lubricating the interface, and reduce the friction and wear. At 450°C, the Raman data suggests that the wear tracks of both the mated surfaces were composed of NiO [38]. This result is consistent with the XPS data from these surfaces.

4 Summary and Discussion

In overview, the goal of this research was to mitigate gross slip fretting wear in Ti6Al4V mated interfaces from room temperature up to 450°C, through the use of nickel graphite composite thermal sprayed coatings. The inclusion of graphite particles into the nickel coating matrix reduced the interfacial friction at both room temperature and 450°C. The combination of microstructural and surface chemistry analysis showed that during the room temperature fretting wear tests, the nickel graphite composite coatings reduced the wear to the mated Ti6Al4V surfaces by minimizing the initial adhesive wear and facilitating the formation of a graphitic transfer film. The NiG-10 coatings were tested as-sprayed, or without surface modification. The inherent surface roughness of the coatings caused the minimal adhesive wear that was observed during the first 10 cycles of wear at room temperature, Fig 15A. During the initial wear cycles, asperities were sheared and a smooth wear track was formed. It was during this phase of wear that the mated Ti6Al4V ellipsoid was damaged. While the asperities were being deformed, the imbedded graphite particles were also sheared and a lubricious graphite transfer film was formed at the interface. Although the graphitic transfer film reduced the coefficient of friction down to 0.35 at room temperature, this is much higher than the traditional 0.2 coefficient of friction that is measured during graphite lubrication. The friction was not able to reach 0.2 because the transfer film is not a purely graphite film, as it contains small amounts Ni_2O_3 and TiO_2 (from the initial wear damage).

Lower friction with the same coating may be possible by burnishing some graphite onto the coating surface prior to fretting or by controlling the coating roughness. Burnishing graphite onto the coating would fill the asperity gaps with graphite and reduced the number of cycles required to form a lubricious graphitic transfer film. Another approach could be to control the asperity sized and distribution during the coating process, or by post process grinding/polishing. A smooth interface may accelerate the graphite transfer film formation by bringing the imbedded graphite particles closer to the initial contact surface.

At 450°C, the initial adhesive wear was minimized further by the formation of a transfer film that was composed primarily of nickel oxide (NiO). Although the surface chemistry does not suggest that graphitic lubrication occurred at the interface, the presence of the carbon has enhanced the formation of a continuous transfer film. The experiments conducted with the commercially pure Ni coatings at 450°C did form a lubricious NiO transfer film, but it was not continuous or uniform. Instead it was patchy with localized regions of wear debris. Therefore, the addition of the embedded graphite particles enhanced the performance of the nickel coatings at both room temperature and 450°C.

5 Conclusions

The use of nickel graphite composite coatings for gross slip fretting wear mitigation was investigated through experimentation, wear morphology, and surface chemistry analysis. From this research it can be concluded that:

- Nickel graphite composite coatings effectively reduced wear on the mated Ti6Al4V surfaces at room temperature and 450°C by the formation of lubricious graphitic and nickel oxide (NiO) based transfer films respectively.
- Compositions of 5% to 20% graphite in the pre-spray powder mixture were similarly effective in reducing the friction between the Ni based thermal sprayed coatings and the mated Ti6Al4V interfaces.
- At 450°C the inclusion of graphite particles in the nickel coatings enhanced the formation of a uniform and continuous NiO based transfer film.
- The presence of nickel trioxide (Ni_2O_3) and titanium dioxide (TiO_2) in the room temperature wear tracks increased the friction of the graphitic transfer films to 0.35, instead of the traditional 0.2 or lower that is typical of graphite based lubrication.

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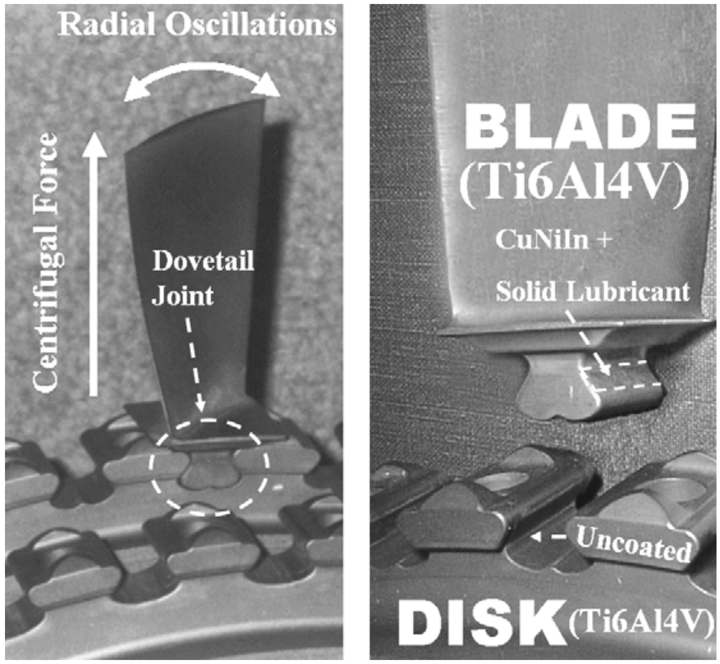

Figure 1. Dovetail joint at the blade/disk interface.

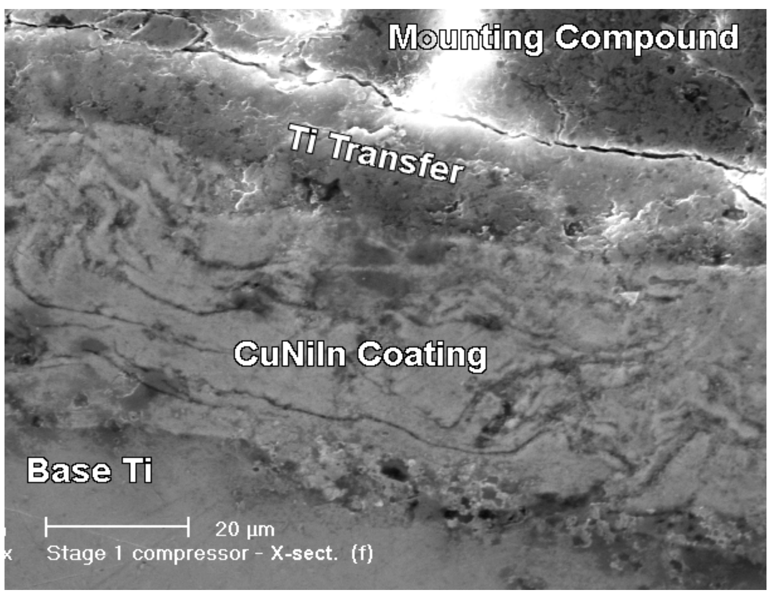

Figure 2. Cross-section of a worn turbine engine compressor blade dovetail [11].

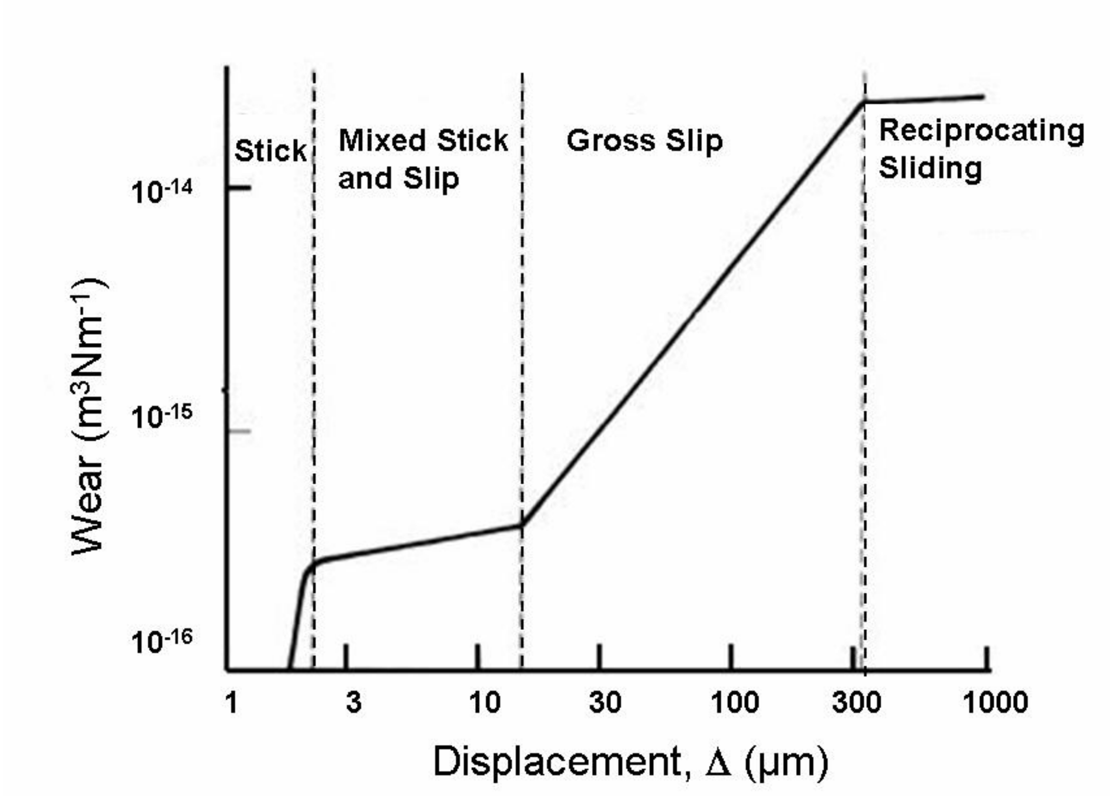

Figure 3. Wear regime example plot using steel on steel with a fixed geometry, constant load, and varied stroke length from I.M. Hutchings, Tribology [23].

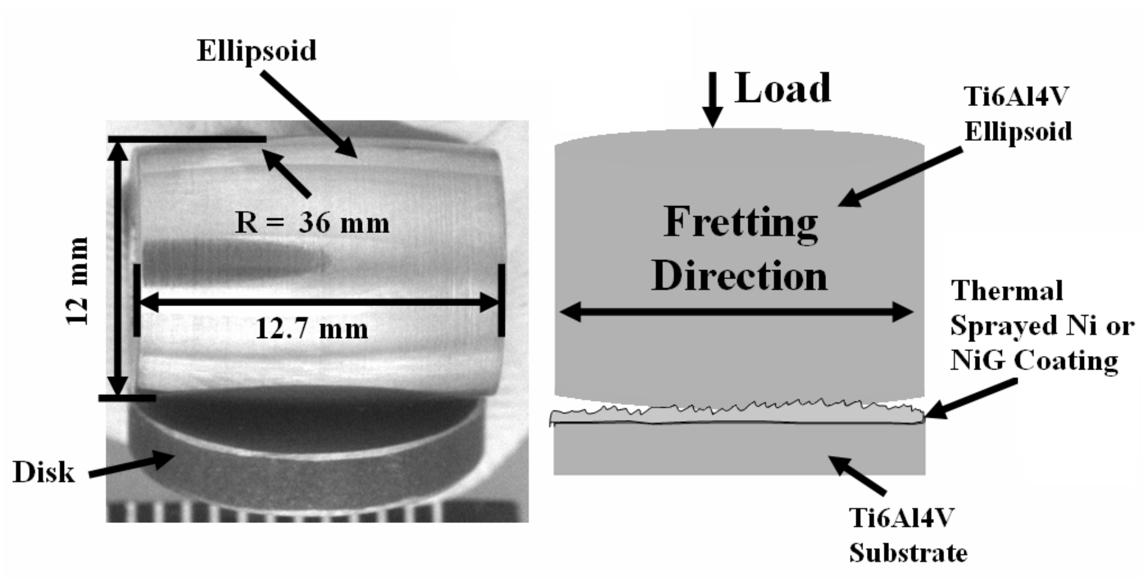

Figure 4. Ellipsoid contact geometry.

Table 1. Substrate and coating properties.

Materials	Composition Weight %	Roughness Ra (μm)	Nano Hardness (GPa)	Micro Hardness (HV)	Modulus (GPa)
Titanium Substrates	90% Ti, 6% Al, 4% V	0.1	4.1	284	143
Copper Nickel Indium	64% Cu, 35% Ni, 1% In	9	2.4	138	90
Nickel	Commercially Pure	7	2.1	133	82

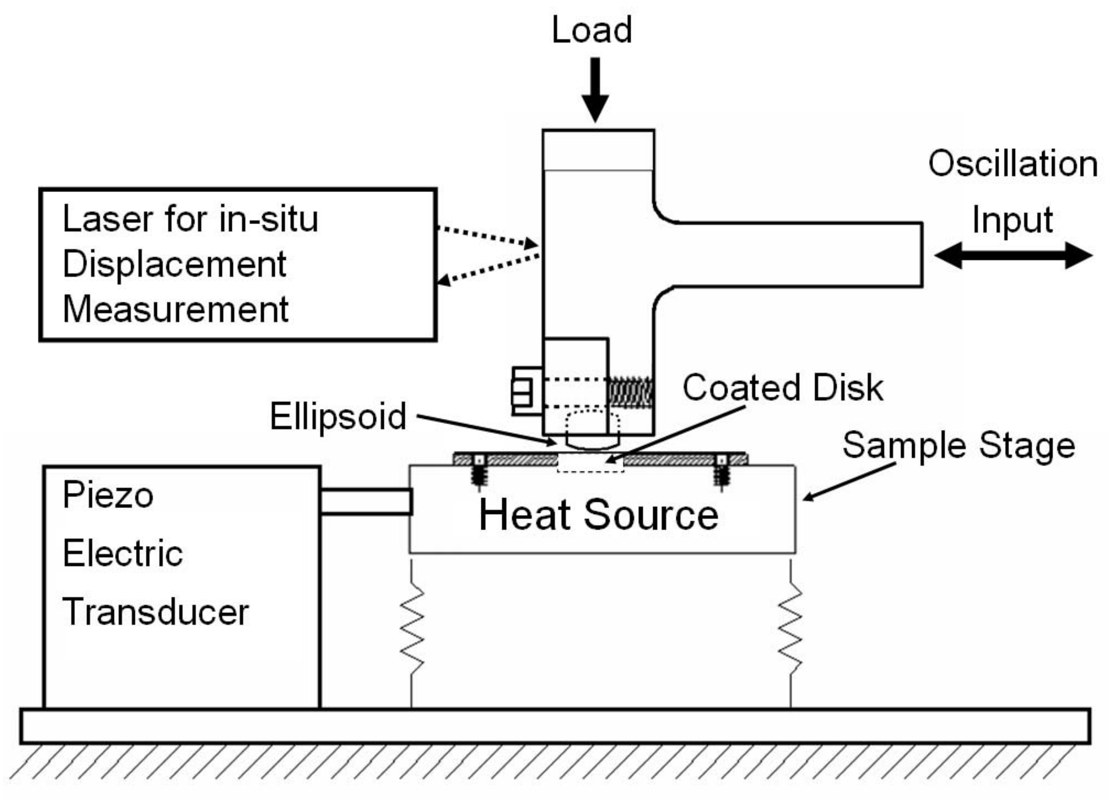

Figure 5. Fretting wear tribometer.

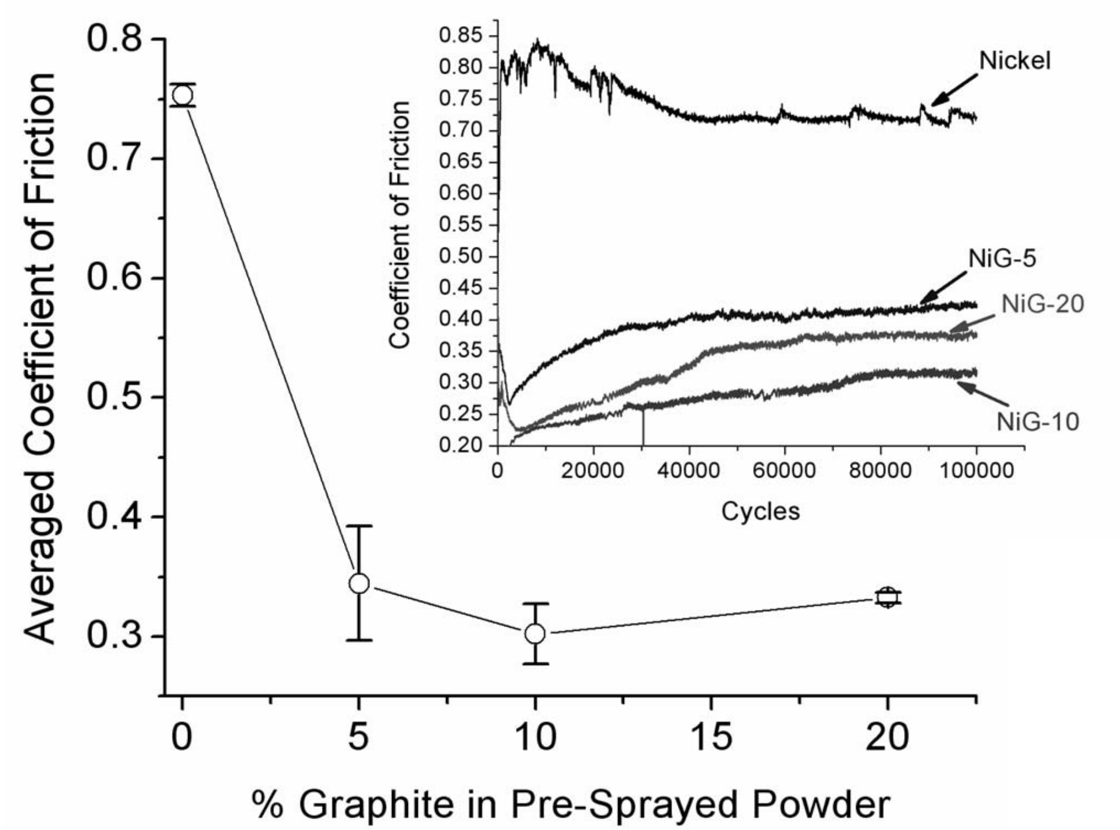

Figure 6. Typical RMS friction data from 30 Hz fretting wear experiments on the thermally sprayed nickel graphite composite coatings with varied graphite composition in the pre-sprayed powder mixtures. The small plot (upper right) is a plot of the typical RMS friction data recorded during any single test. The large plot is the average of 4 experiments conducted on each coating composition.

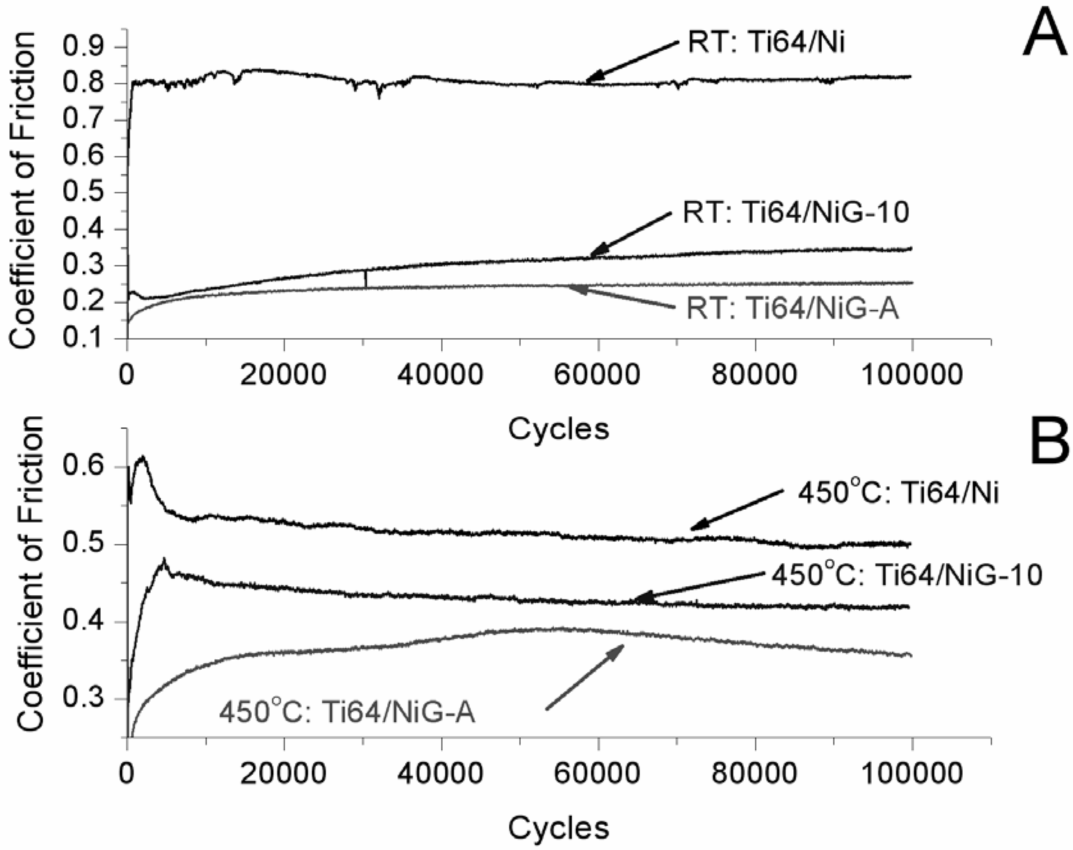

Figure 7. Typical RMS friction data from 30 Hz fretting wear experiments. Data in (A) is from experiments conducted at room temperature, and data in (B) is from experiments conducted at 450°C.

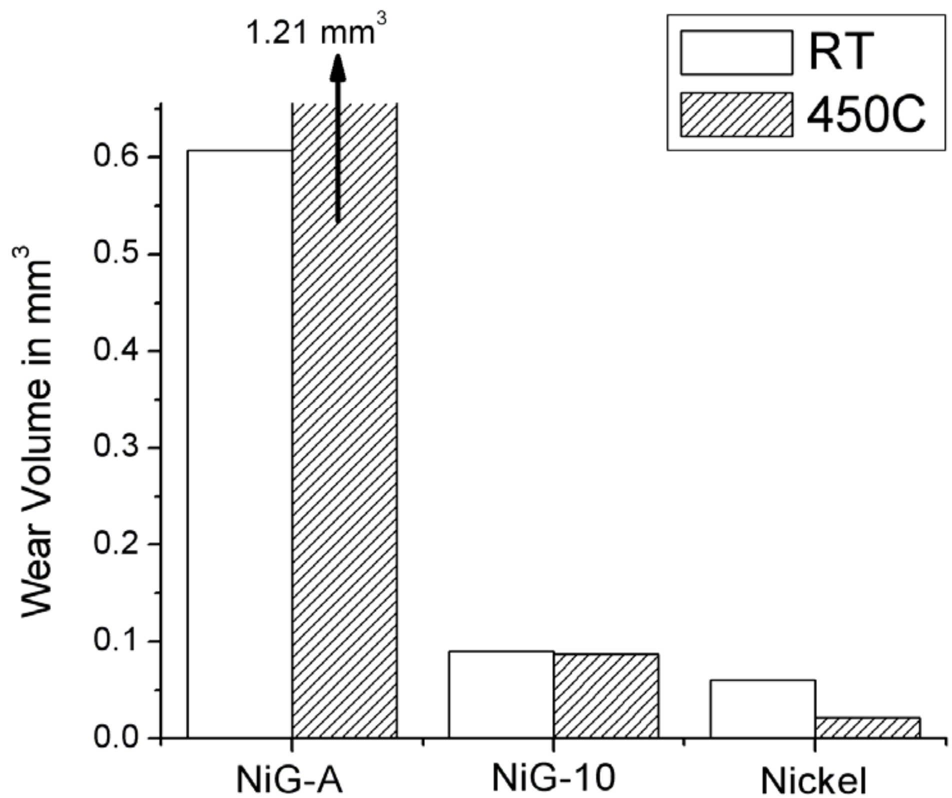

Figure 8. Average wear volume in the fretting wear tracks on the thermal sprayed coatings after experiments conducted at room temperature and 450°C.

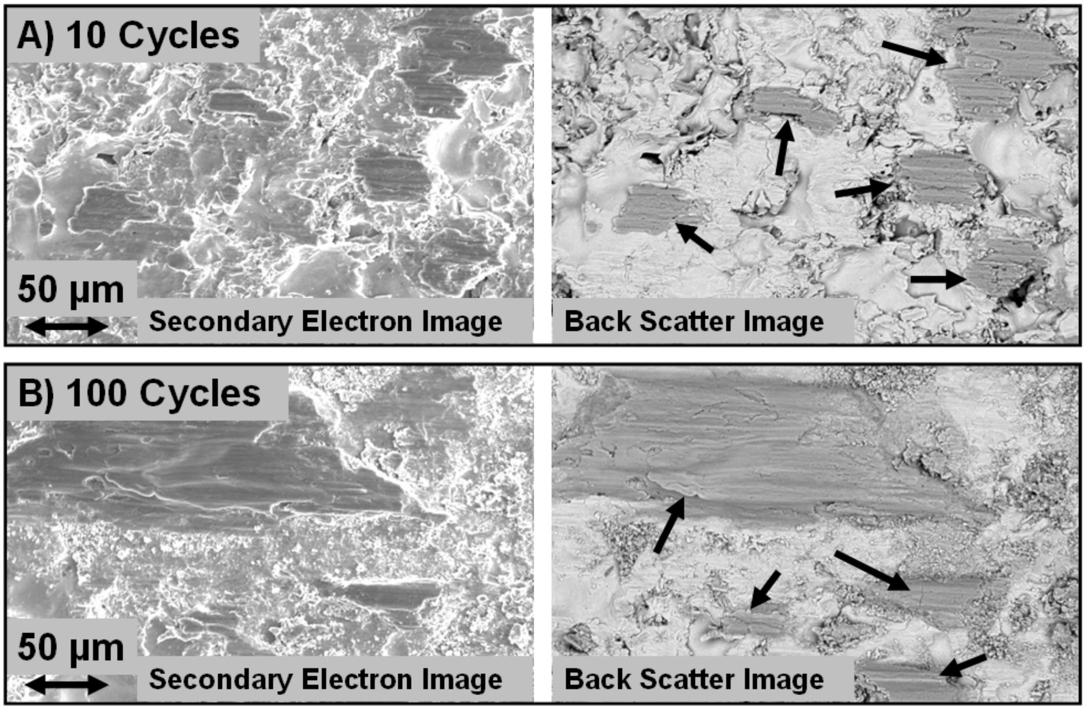

Figure 9. Magnified secondary electron and back scatter images of the boxed regions in the Ni coating wear tracks shown in Fig 11A and 11B. Arrows point to dark regions that were identified as Ti-alloy using energy dispersive spectroscopy.

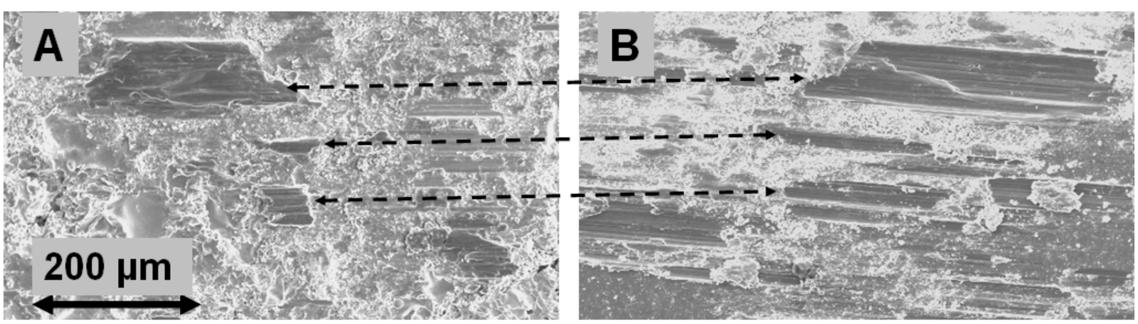

Figure 10. Side by side images of the Ni coating and Ti6Al4V mated wear tracks after 100 cycles of fretting wear at room temperature. The arrows show directly where the adhered Ti6Al4V in A) was removed from the surface in B).

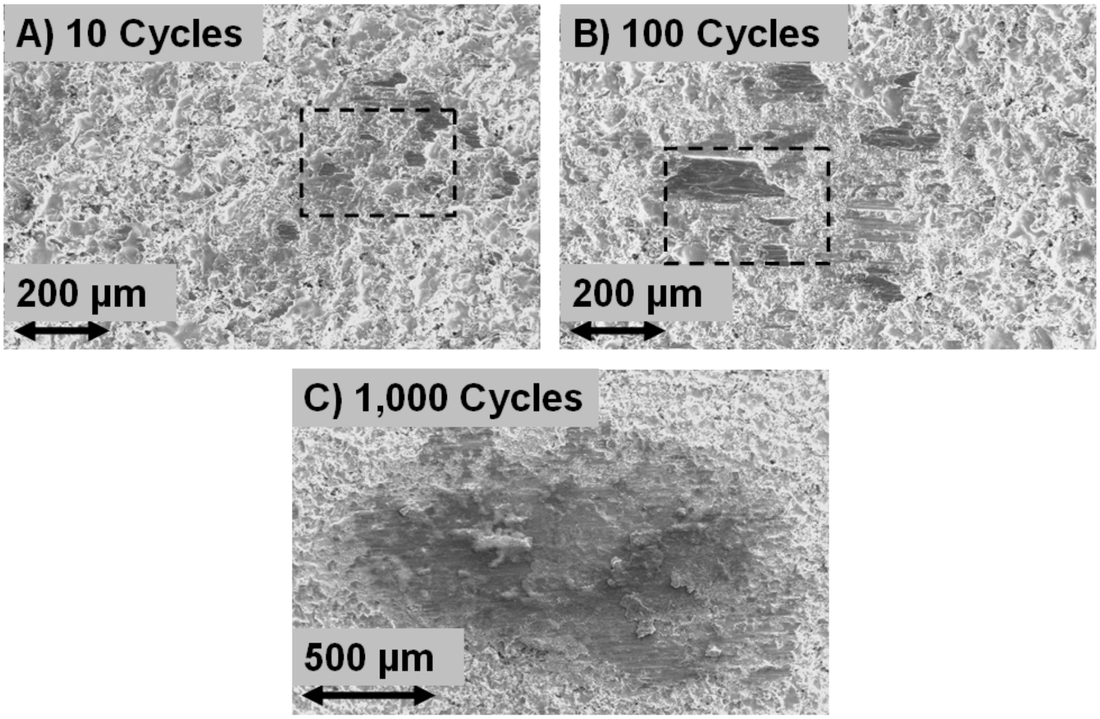

Figure 11. Images of the Ni coating tested at room temperature after A) 10 cycles, B) 100 cycles, and C) 1,000 cycles against an uncoated Ti6Al4V ellipsoid.

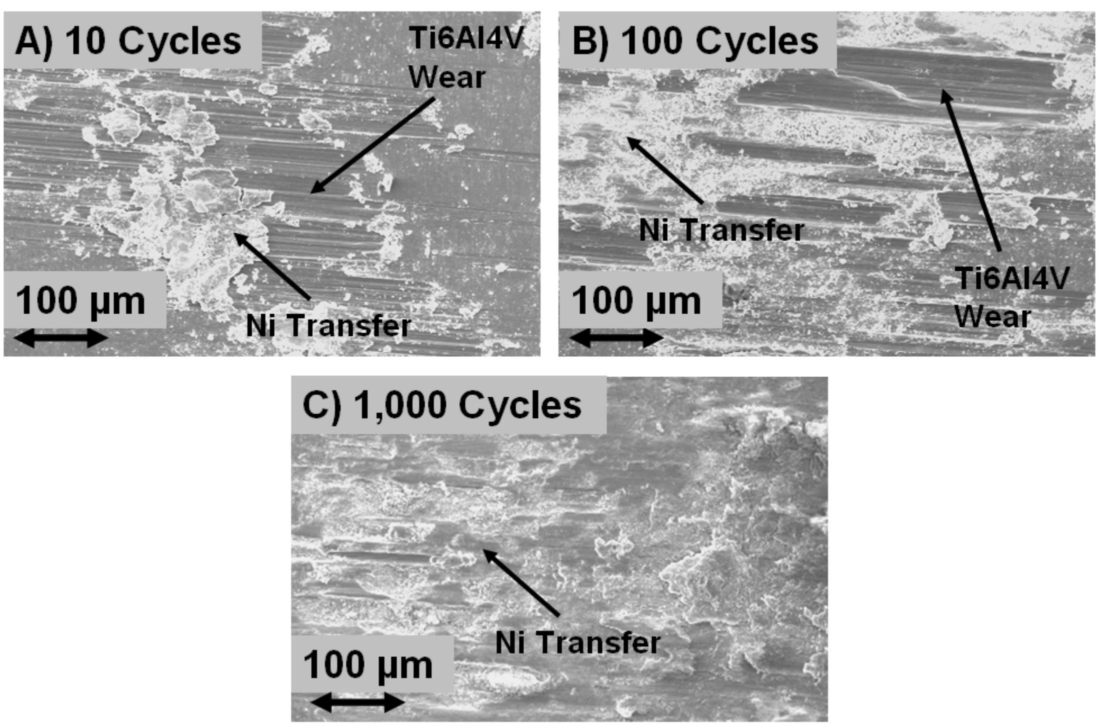

Figure 12. A cyclic accumulation of fretting wear damage on the surface of the Ti6Al4V ellipsoid mated with the Ni surfaces depicted in Fig 9 respectively.

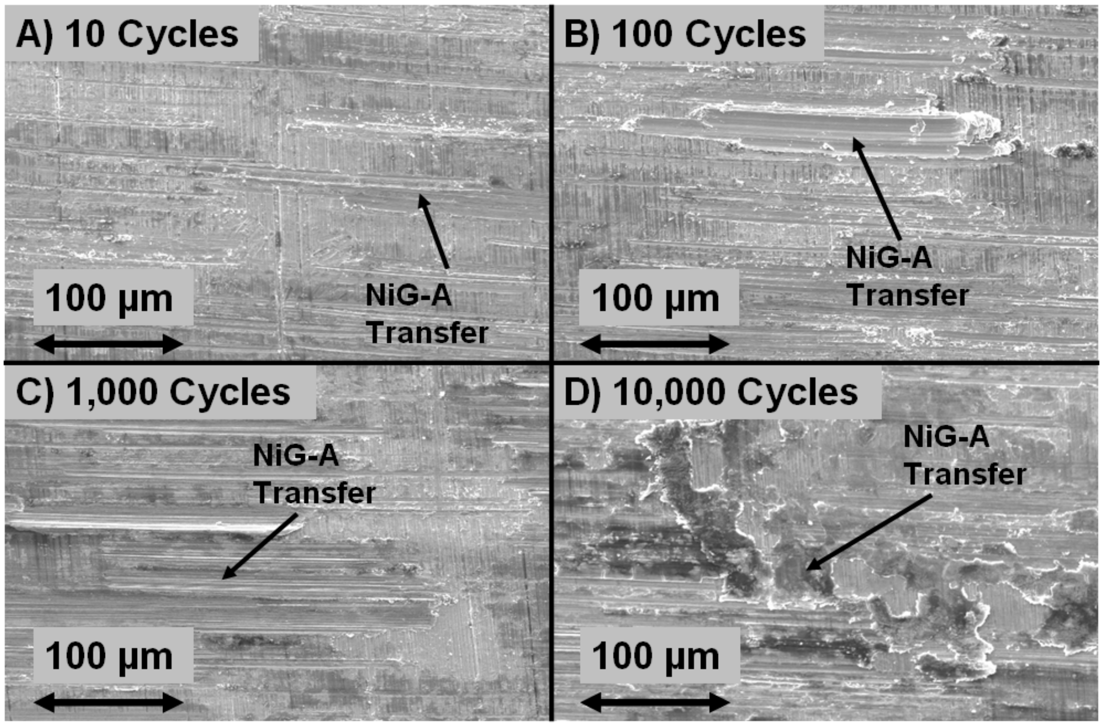

Figure 13. Ti6Al4V wear track images after A) 10 cycles, B) 100 cycles, C) 1,000 cycles, and D) 10,000 cycles against the NiG-A composite coating at room temperature.

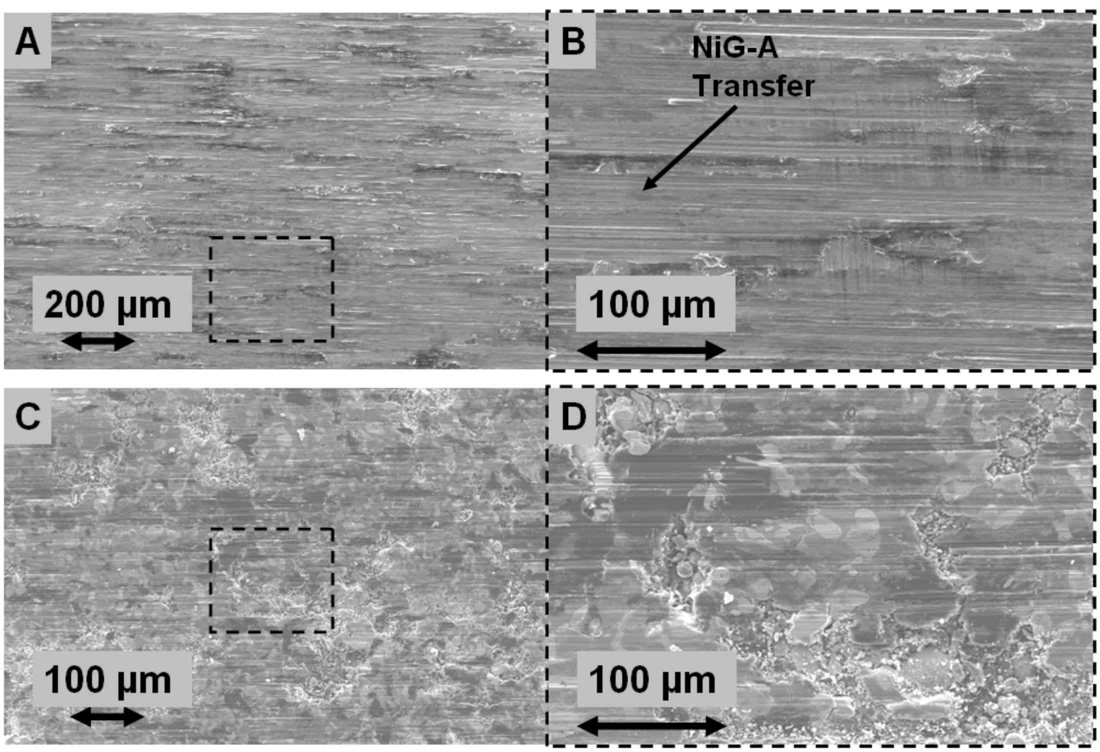

Figure 14. Ti6Al4V (A and B) and NiG-A (C and D) wear track images after 100,000 room temperature fretting wear cycles. The images on the right are magnifications of the boxed regions on the left.

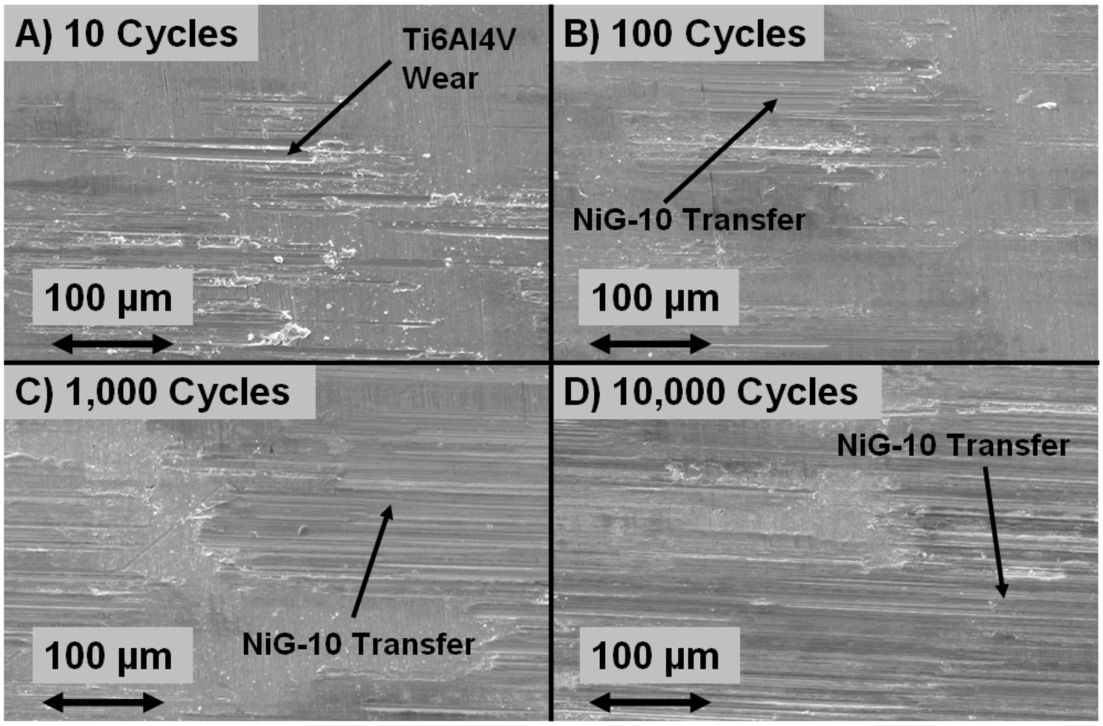

Figure 15. Ti6Al4V wear track images after A) 10 cycles, B) 100 cycles, C) 1,000 cycles, and D) 10,000 cycles against the NiG-10 composite coating at room temperature.

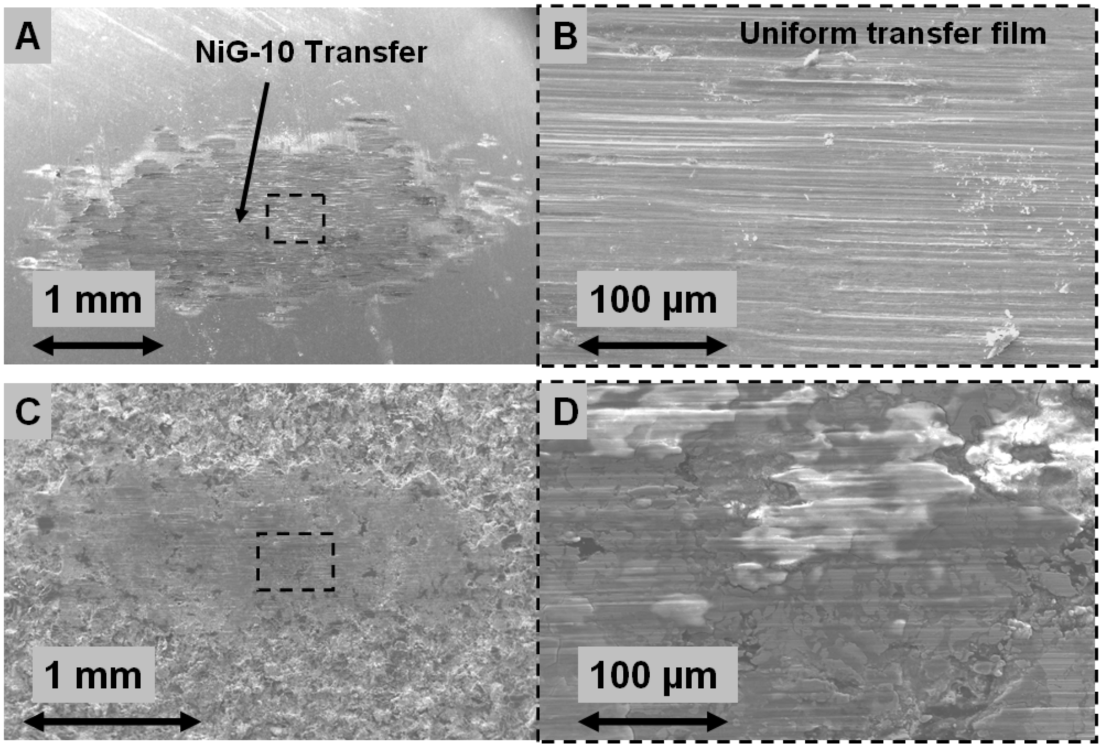

Figure 16. Ti6Al4V (A and B) and NiG-10 (C and D) wear track images after 100,000 room temperature fretting wear cycles. The images on the right are magnifications of the boxed regions on the left.

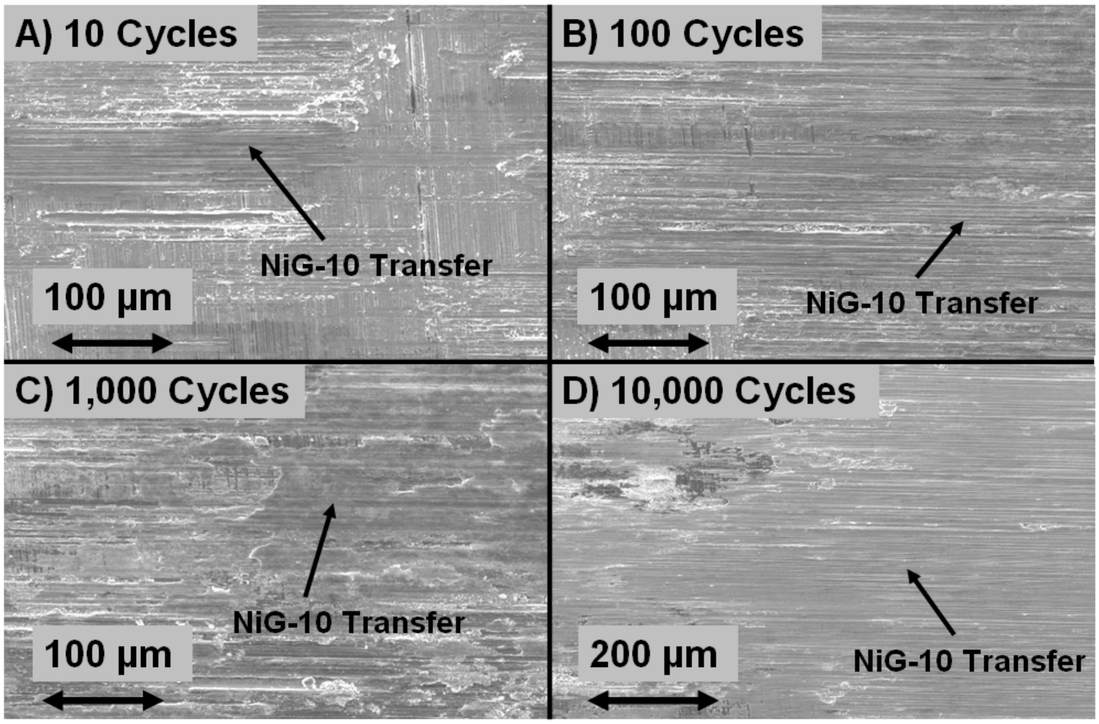

Figure 17. Ti6Al4V wear track images after A) 10 cycles, B) 100 cycles, C) 1,000 cycles, and D) 10,000 cycles against the NiG-10 composite coating at 450°C.

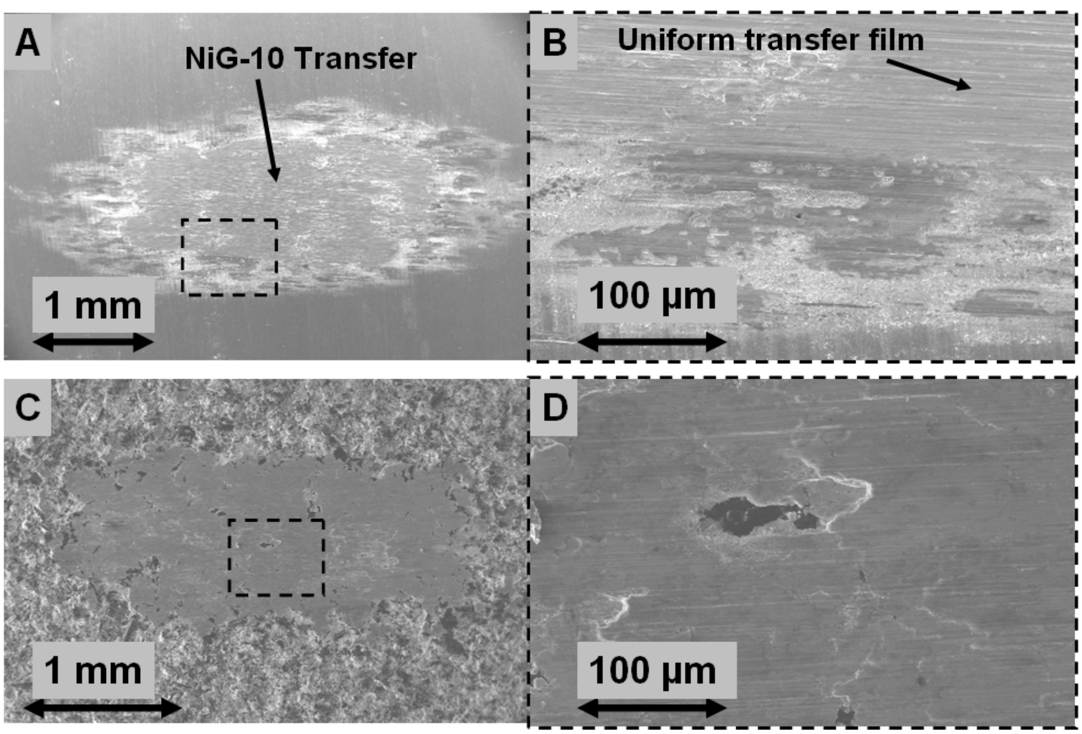

Figure 18. Ti6Al4V (A and B) and NiG-10 (C and D) wear track images after 100,000 fretting wear cycles at 450°C. The images on the right are magnifications of the boxed regions on the left.

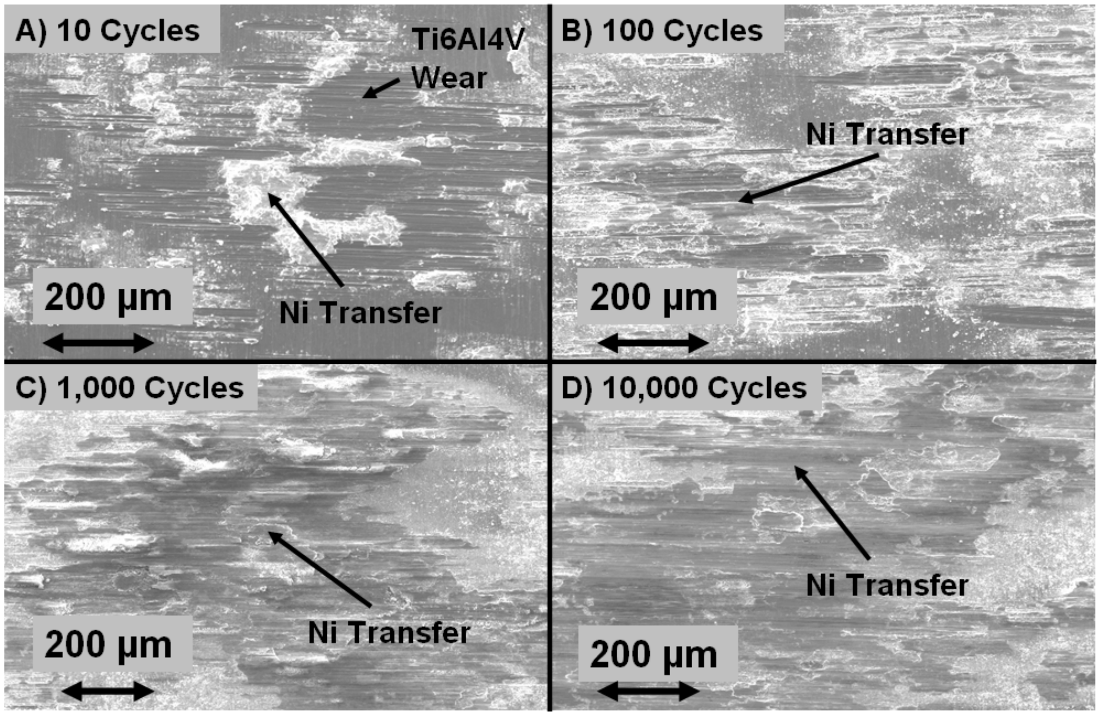

Figure 19. Ti6Al4V wear track images after A) 10 cycles, B) 100 cycles, C) 1,000 cycles, and D) 10,000 cycles against the commercially pure Ni coating at 450°C.

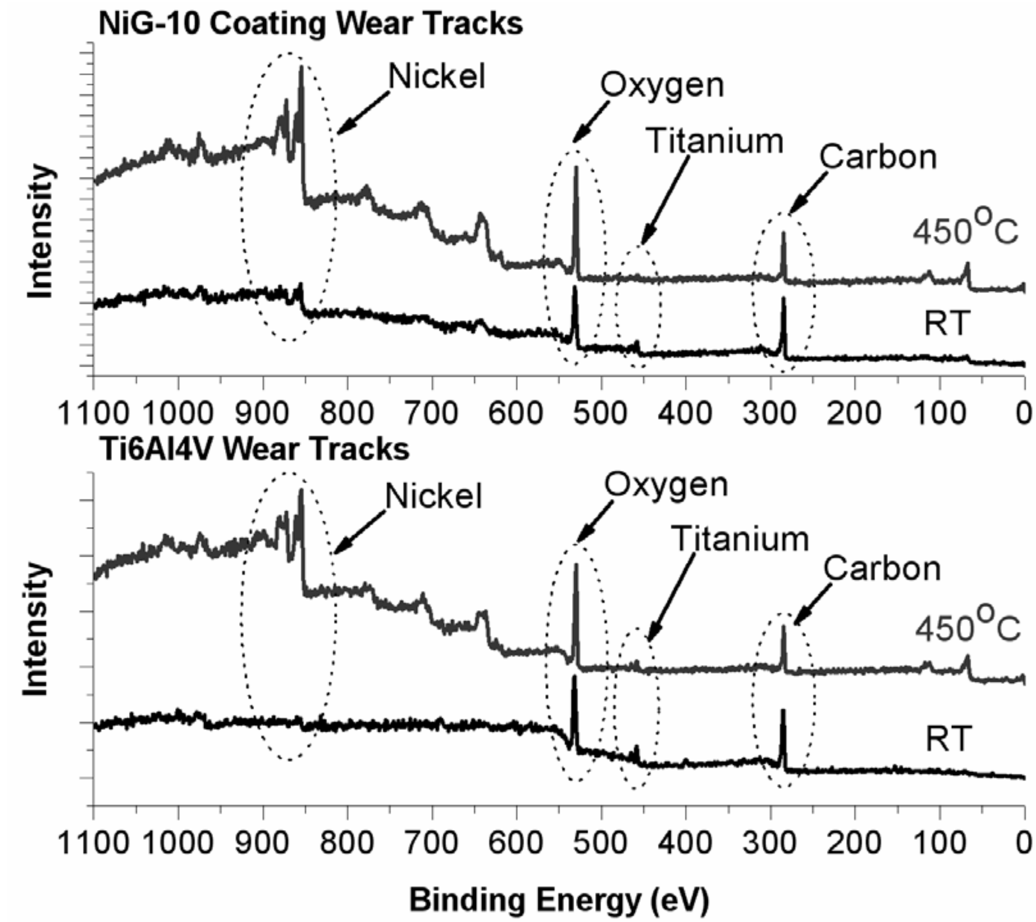

Figure 20. XPS survey scans in the fretting wear tracks of samples tested at room temperature (RT) and 450°C after 10,000 cycles.

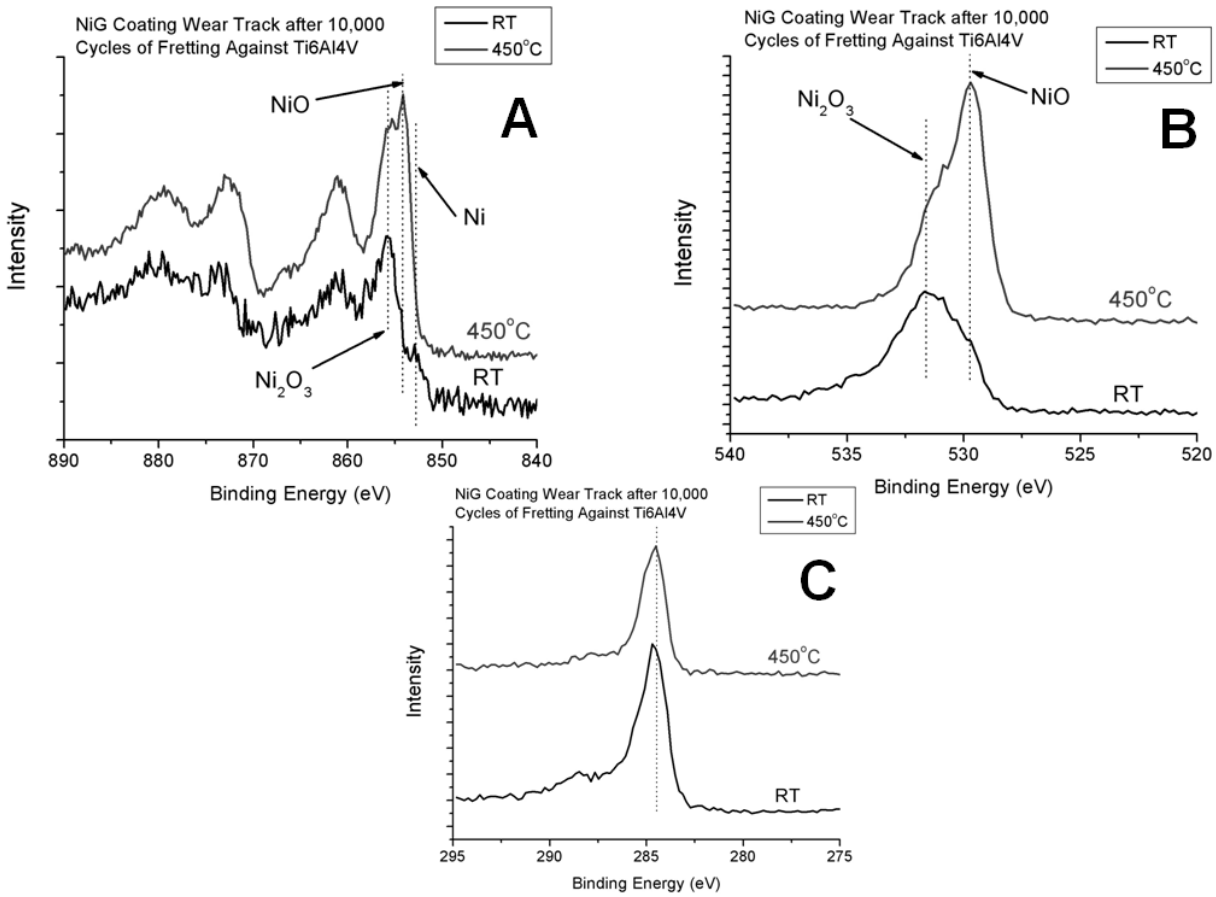

Figure 21. High resolution XPS scans in the NiG-10 coating wear tracks of samples tested at room temperature (RT) and 450°C after 10,000 cycles. A) Shows the Ni 2p peaks. B) Shows the O 1s peaks. C) Shows the C 1s peak.

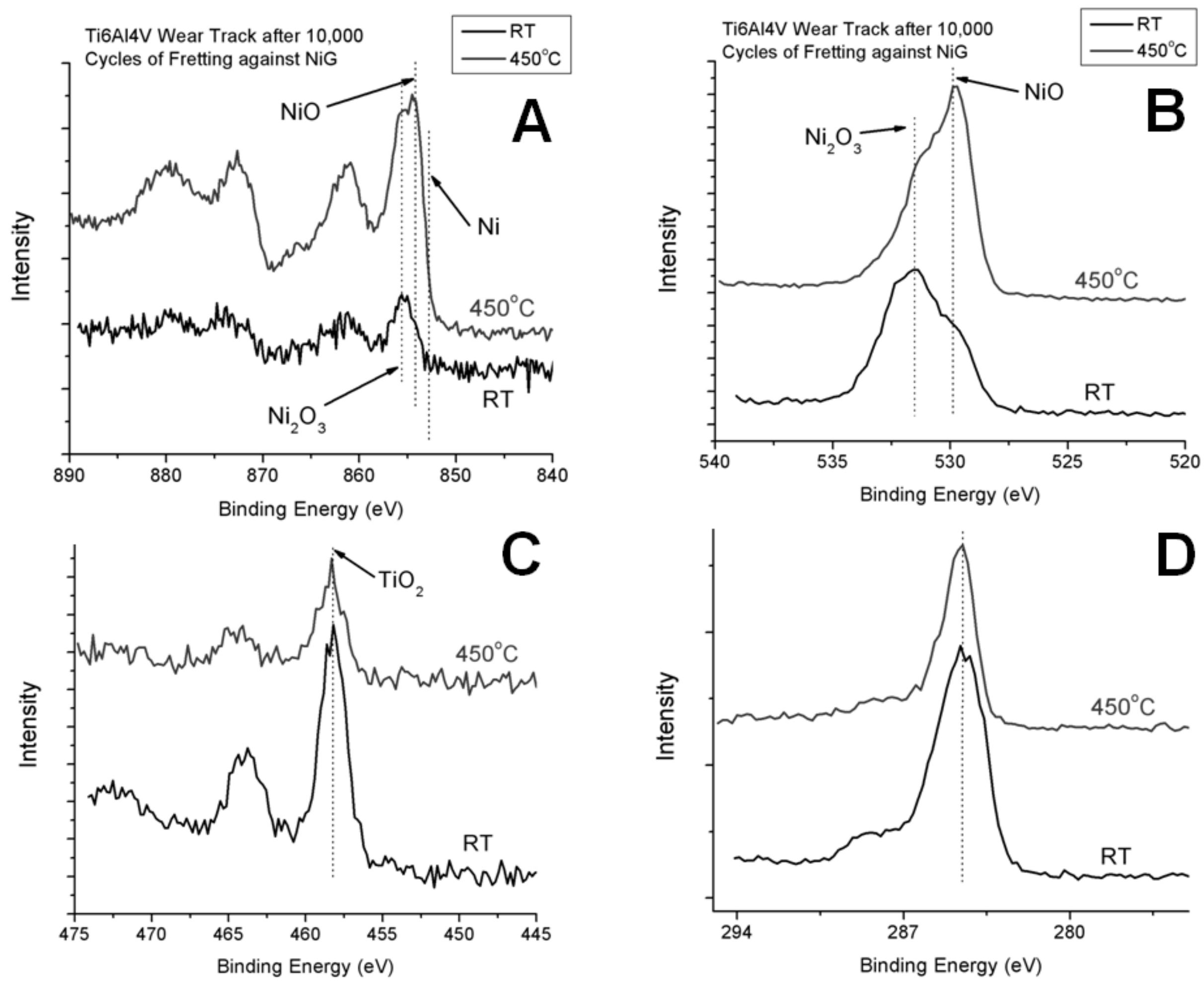

Figure 22. High resolution XPS scans in the Ti6Al4V ellipsoid fretting wear tracks of samples tested at room temperature (RT) and 450°C after 10,000 cycles. A) Shows the Ni 2p peaks. B) Shows the O 1s peaks. C) Shows the Ti 2p peaks. D) Shows the C 1s peak.

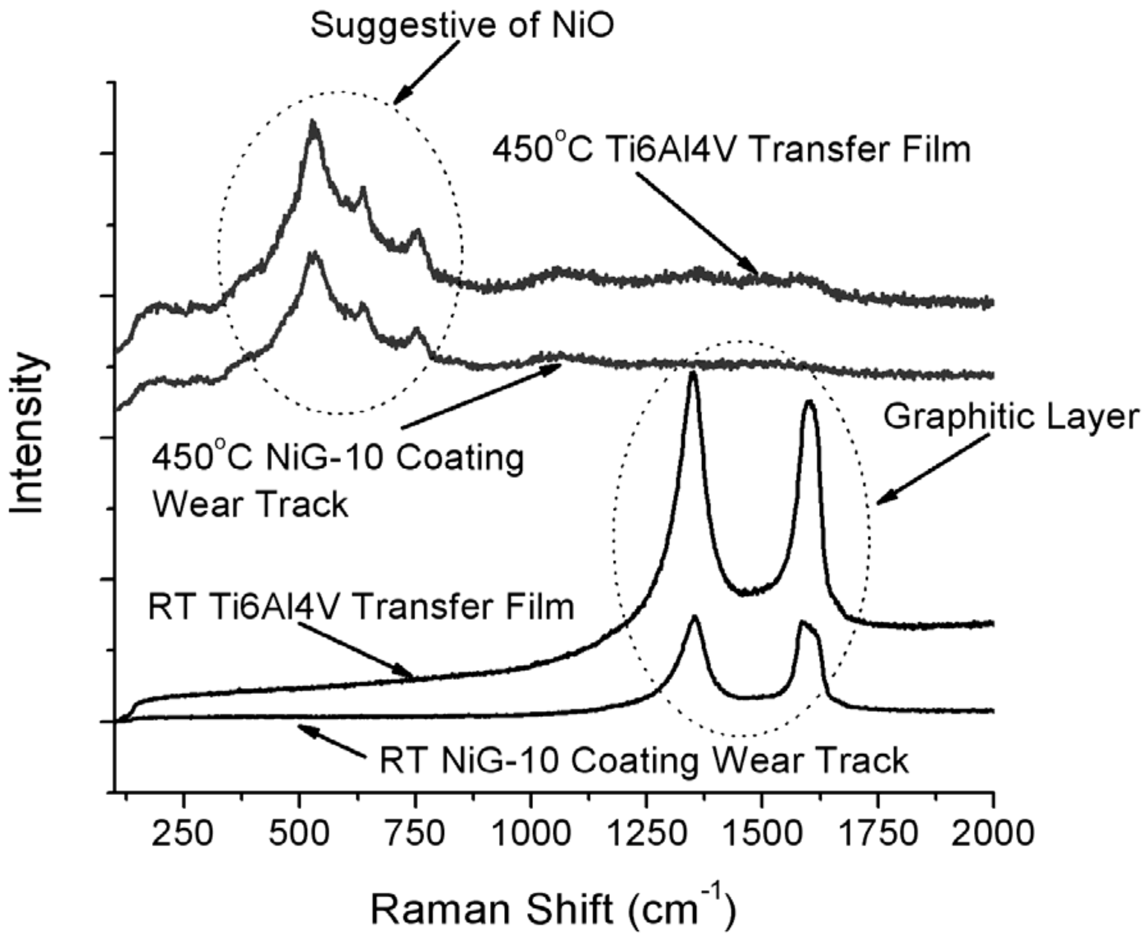

Figure 23. Raman laser spectroscopy scans in the fretting wear tracks of samples tested at room temperature (RT) and 450°C after 10,000 cycles.