

Characterization of ion beam modified ceramic wear surfaces using Auger electron spectroscopy

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An investigation of the surface chemistry and morphology of the wear surfaces of ceramic material surfaces modified by ion beam mixing has been conducted using Auger electron spectroscopy and secondary electron microscopy. Studies have been conducted on ceramic/ceramic friction and wear couples made up of TiC and NiMo-bonded TiC cermet pins run against Si_3N_4 and partially stabilized zirconia disc surfaces modified by the ion beam mixing of titanium and nickel, as well as unmodified ceramic/ceramic couples in order to determine the types of surface changes leading to the improved friction and wear behaviour of the surface modified ceramics in simulated diesel environments. The results of the surface analyses indicate that the formation of a lubricating oxide layer of titanium and nickel, is responsible for the improvement in ceramic friction and wear behaviour. The beneficial effect of this oxide layer depends on several factors, including the adherence of the surface modified layer or subsequently formed oxide layer to the disc substrate, the substrate materials, the conditions of ion beam mixing, and the environmental conditions.

1. Introduction

An ongoing study of the friction and wear of ceramic materials is being conducted to determine the feasibility of their application in high temperature adiabatic engines [1]. It has been found, on the basis of short term pin-disc tests, that disc surfaces modified by ion beam mixing with titanium and nickel showed better friction and wear characteristics (low coefficients of friction, μ_F , minimal material loss in the wear tracks) than those discs not surface treated or those surface ion beam mixed with chromium, when tested in atmospheres similar to those found in diesel engines [1]. It is obvious that the conditions present and the processes occurring at the interfaces between the pins and discs determine the wear characteristics of the various ceramic pin-disc combinations. The purpose of this exploratory surface study was to determine the differences between the surface characteristics of pin-disc combinations showing good wear properties and those showing less favourable wear properties.

2. Experimental procedure

The pins and discs analysed in this study are listed in Table I. The details of the wear experiments are given in [1]. Pin-disc combinations 1 and 4 showed the best wear characteristics of those investigated in the wear study [1]. Pin-disc combinations 2 and 3 showed less favourable wear characteristics and a possible role of pin material in the wear process. These four pin-disc combinations were therefore chosen for extensive analyses using Auger electron spectroscopy (AES). The results of AES or energy dispersive spectroscopy

(EDS) analyses of the surfaces of other pin-disc combinations showing poorer wear characteristics will be discussed as necessary.

The investigations of the wear surfaces of both pins and discs listed in Table I were performed with a PHI 595 scanning Auger electron microscope. While AES is now used routinely to investigate surface properties of metals, there are still unresolved problems when it comes to dealing with bulk semiconducting, or in this case, nonconducting materials. These include charging of the materials due to the accumulation of positive or negative charge at the analysed region [2, 3], and alteration of the analysed surface by the electron beam, or by the ion beam during sputtering [3, 4].

The problem of charging can manifest itself in two ways in scanning Auger microscopy: electrostatic charging which disturbs the secondary electron image as commonly found in secondary electron microscopy (SEM) [5], and charge induced shifts in Auger peak positions [2, 3, 6]. The charging of insulating samples is due to their inability to remove excess charge by conduction. In the case of electron microscopy, excess charge is created through the production of secondary electrons by the incident beam. The dependence of the secondary electron yield, δ , on the primary electron energy is shown schematically in Fig. 1. The energy range of interest for AES is that between the two crossover points, E_1 and E_2 , where $\delta > 1$ [3, 6]. In this range, however, a net positive charge will build up at the surface of an insulating specimen because more electrons leave the specimen than are incident on it. This positive charge will retard

TABLE I Pin-disc combinations tested in diesel (O, N, CO₂, H₂O) environment at 800°C*

Disc [†]	Pin [†]	μ_F
1 Silicon nitride Si ₃ N ₄ (Ti, Ni)	TiC	0.09
2 Silicon nitride Si ₃ N ₄ (Ti, Ni)	TiC-5Ni-5Mo	0.22
3 Partially stabilized zirconia PSZ (Ti, Ni)	TiC	0.25
4 Partially stabilized zirconia PSZ (Ti, Ni)	TiC-5Ni-5Mo	0.09

*The elements given in parentheses are those ion-beam mixed into the surfaces of the discs.

[†]Specimen dimensions: Disc diameter = 7.62 cm; thickness = 0.95 cm. Pin diameter = 0.64 cm; length = 1.27 cm.

the emitted Auger electrons and therefore cause a shift of the Auger peak heights to lower energies [6]. This will cause little problem with normal elemental identification since surface charging should affect all Auger peak positions by the same amount. Some caution should be exercised, however, in analysing Auger spectra for chemical information related to peak energy shifts. By considering the changes in the differences between Auger peak positions, rather than the absolute value of the peak positions, as well as the peak shapes, chemical binding information can still be obtained. However, alteration of surface chemistry by ionic drift as well as by electron beam heating must still be accounted for [3, 4].

Several methods can be used to reduce the problem of charging of insulating specimens, although these require some sacrifice in resolution and sensitivity. The energy range E_1 to E_2 generally falls below 2 kV for such materials and therefore indicates that primary beam energies lower than those normally used for conducting specimens should be used [6]. Reducing the irradiation dosage ($C\text{ cm}^{-2}$) either by reducing the primary beam current or the analysis time can delay the onset of the maximum charging effect as well as the onset of electron beam-induced damage [7]. Reducing the angle of incidence results in a reduction of the secondary emission yield at a given beam condition, thus reducing charging [3, 7]. Non-beam related methods include coating the specimen in a conductor such as gold or silver while masking off a small area for analysis [5, 8], or bombarding the specimen with a neutralizing beam [6]. The neutralizing beam concept is also used for the reduction of charging during ion sputtering [6].

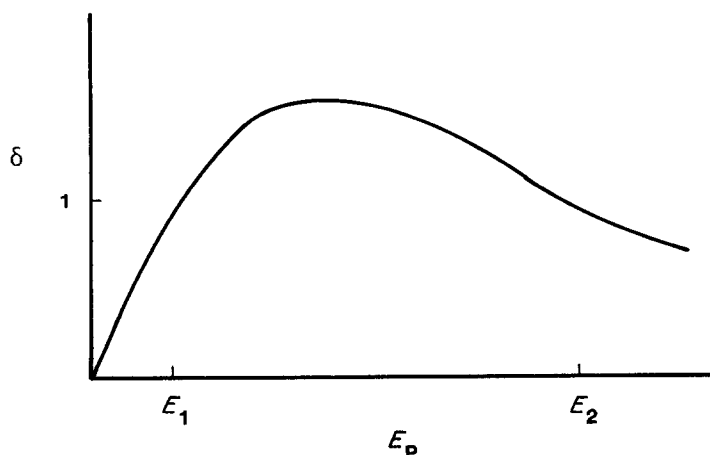


Figure 1 Schematic diagram of secondary electron yield as a function of primary beam energy.

Alteration of specimen surfaces, either conducting or nonconducting by the electron beam or ion beam sputtering can occur by electron beam reduction of the surface [7], migration of ionic species by charge build-up [4], beam heating [4, 7], and preferential sputtering [9]. These problems will have an important effect on the interpretation of quantitative and chemical Auger data. The results of this preliminary study are not greatly influenced by the surface alteration problems, but ongoing work on the fundamental mechanisms of these wear processes requires careful consideration of these issues.

The major consideration for this study was the problem of surface charging. Use of primary beam energies above 2 kV and beam currents above about 10^{-8} A resulted in secondary image distortion, and distortion of the low energy end of the Auger spectra, as well as random spiking throughout the spectra. It was found that a combination of the previously mentioned remedies could reduce the charging problem to a maximum shift of ~ -5 eV in the Auger spectra.

In the case of the discs, a thin film of silver was first vapour deposited on the specimens. It was found that sputtering away an analysis area with concurrent elemental analysis was better than masking, since even a small uncoated area seemed to charge up quickly. The specimens were then tightly wrapped in aluminium foil with a small area left uncovered for analysis, strapped to a specimen holder with copper wire, and mounted in the chamber. The discs were analyzed at the 60° angle of incidence set by the specimen holder in the 595 system at a primary beam energy of 1.5 kV, a beam current of $\leq 5 \times 10^{-9}$ A and a beam size of < 450 nm. To avoid further charging, the beam was blanked while preliminary data handling and analysis was being performed. Depth profiling was performed using argon ion sputtering with a beam energy of 2 kV, current density of $\sim 70 \mu\text{A cm}^{-2}$ and a $2\text{ mm} \times 2\text{ mm}$ raster size. The sputtering rate for the combination of materials used in this study was not known, and the depth scale is therefore given as sputtering time. Use of these sputtering conditions on a Ta₂O₅ film, however, gave a sputter rate of about 11.0 nm min^{-1} .

Because of the small size of the worn area of the pins and the fine scale of the features found there, the pins were not silver coated. They were, however, wrapped in aluminium foil, leaving the worn end uncovered.

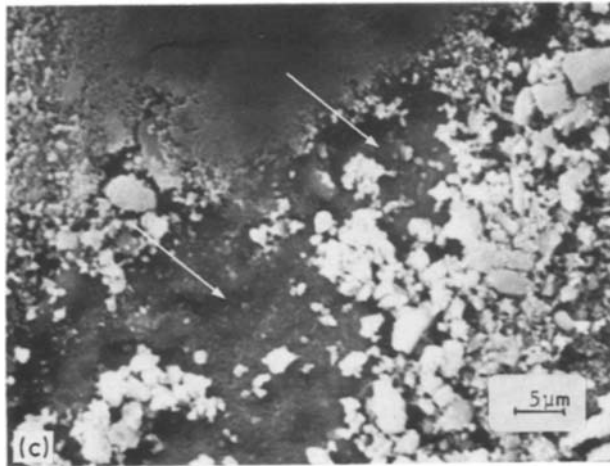
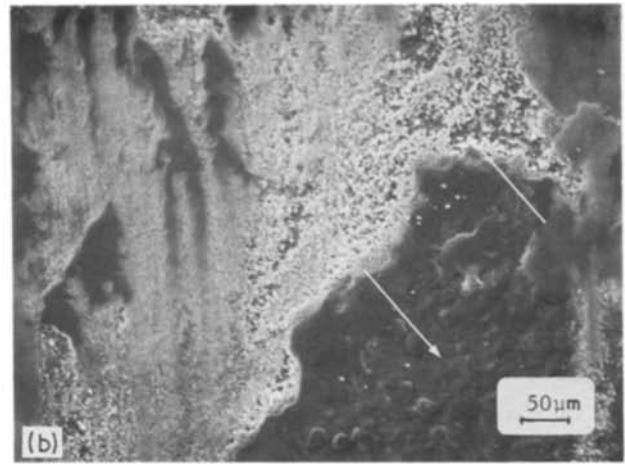
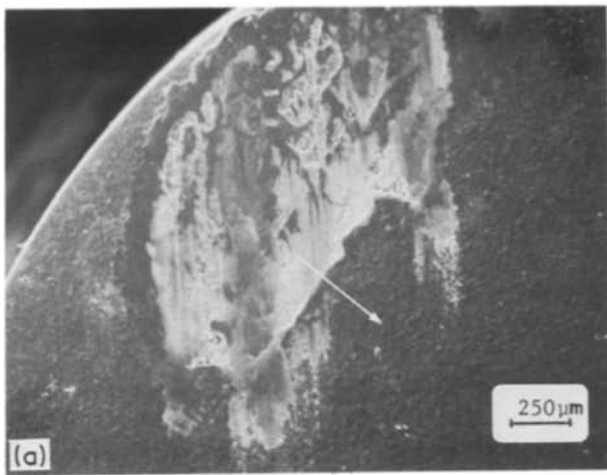


Figure 2 Transfer layer on a TiC pin run against a TiNi-surface modified disc in a diesel environment at 800°C. Arrows indicate pin "base" material.

Examination at glancing incidence of the electron beam was required to avoid charging problems.

3. Results

3.1. Pins

All of the pins which were analysed in this study exhibited a sort of burnish mark where the pin was in contact with the disc. The burnish mark of the pins with higher values of coefficient of friction, μ_F , were larger than those with the low values of μ_F . A typical burnish mark from a TiC pin run against a Si_3N_4 (Ti, Ni) disc (low μ_F couple) is shown in Fig. 2a. It appears that the burnish mark is actually a layer of material which was transferred from the disc to the pin, and was then broken up later in the wear run. This is more clearly seen at higher magnification in Figs 2b and c. Arrows indicate areas (usually darker) where the pin "base" material appears beneath the burnish layer. This mark will thus be referred to from this point on as a "transfer layer".

Typical Auger spectra from the unworn surface of the pin and the transfer layer are shown in Figs 3a–d. The main difference between the two areas, as seen by comparing Figs 3a and b with Figs 3c and d, is the presence of nickel on the transfer layer. Since these spectra come from the TiC pin, the nickel could only have transferred from the TiNi modified disc to the pin. It is not clear whether or not the nickel is present in the oxidized state, because the peak energy and shape changes associated with the oxidation of nickel are too small to be resolved considering the present

specimen and beam conditions [10]. Titanium is present in the oxidized state as evidenced by the absence of the elemental Ti(27 eV) peak and the presence of the oxidized Ti(40 eV) peak [11], and the fact that the Ti(387 eV) peak is larger than the Ti(418 eV) peak [11–14].

Carbon is also present in significant amounts, with a greater amount of carbon being found on the transfer layer (Fig. 3a) than on the unworn surface (Fig. 3c) as indicated by the larger peak height ratio $\text{C}(272 \text{ eV})/\text{O}(510 \text{ eV})$ for the transfer layer. Sputtering of the pin surface resulted in a reduction of the carbon signal with depth while the titanium oxide peaks remain strong. However, the presence of a small amount of carbon even after 30 min of sputtering indicates that this carbon layer consists of more than just carbon adsorbed during specimen handling. While the TiC pin is probably oxidized to a significant depth, this relatively thick carbon layer is probably the result of the interaction of the diesel environment with the pin surface, although some transfer of carbon originally ion beam mixed in the discs is also a possibility (see next section). The apparently higher surface concentration of carbon on the transfer layer would be due to the higher temperatures existing at the contact point, and/or the direct contact with the carbon containing modified layer on the disc.

The results for the other pins shown in Table I were similar to those for the TiC pin just described. The TiC–Ni–Mo pin run against Si_3N_4 (couple 2), had however a much higher nickel signal on the transfer layer, as well as having nickel on the unworn area. The transfer layer was much larger than even the other high μ_F pin (couple 3) and could account for some smearing of nickel onto the unworn areas. Since μ_F for this pin is the same as that for the TiC pin of couple 3, it is suspected that this difference could be related to slight variations in the orientation between the pin surfaces and the discs.

While little difference was found between the pin surfaces except as mentioned above, it appears that the pin composition could have played a role in the wear characteristics, although in a contradictory

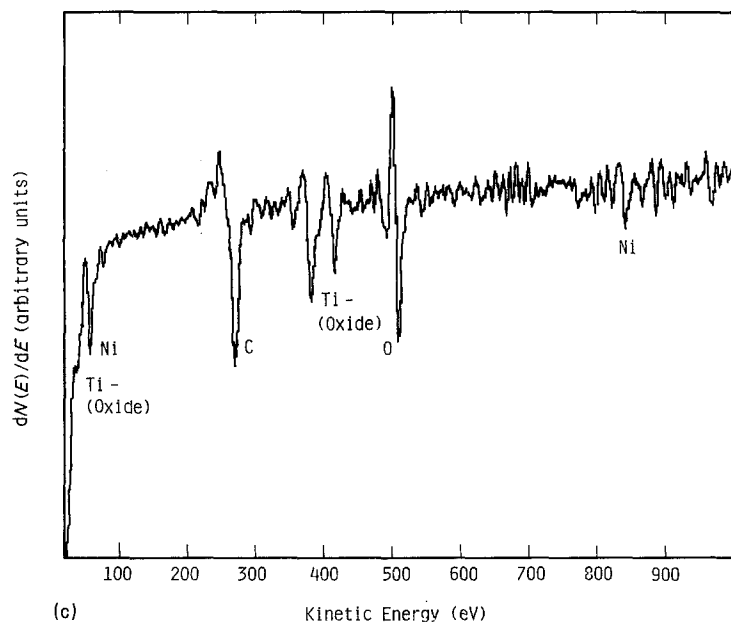
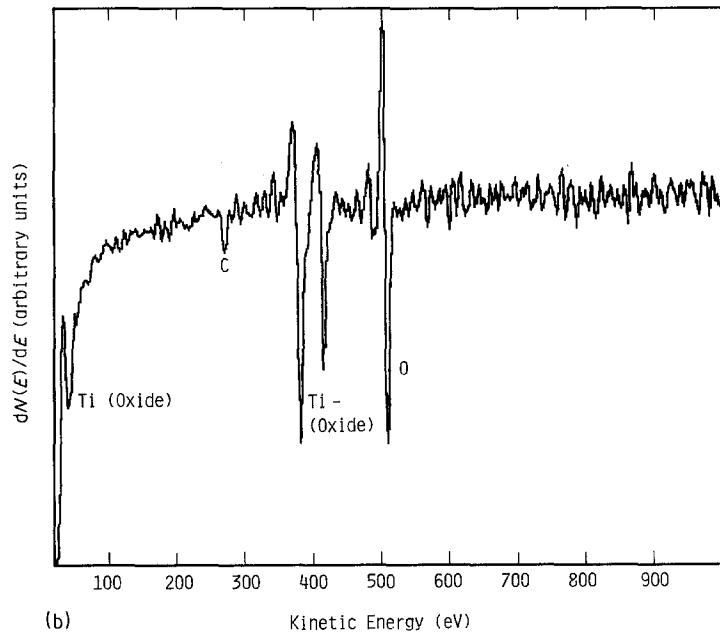
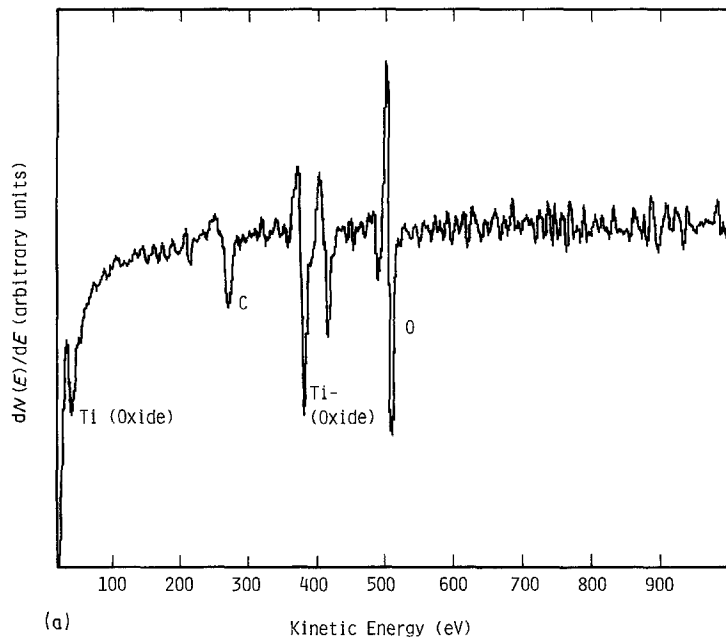
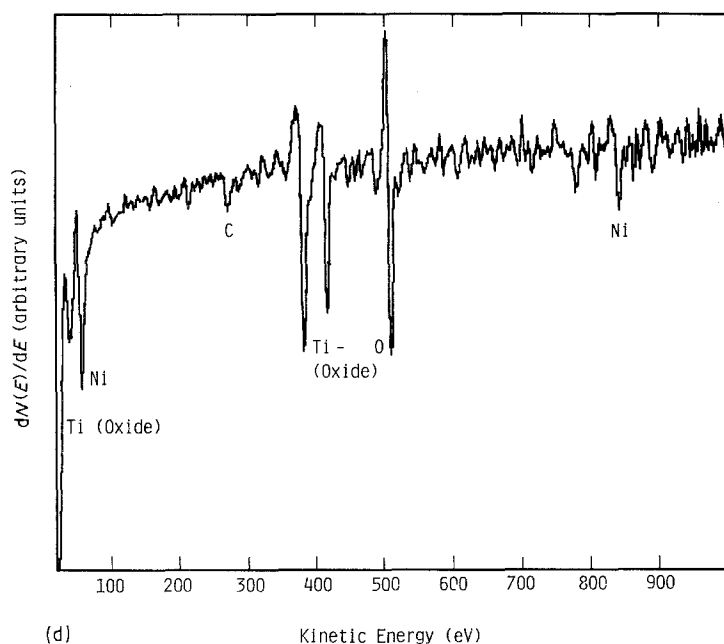


Figure 3 Auger spectra taken from a TiC pin run against a TiNi surface modified Si_3N_4 disc in a diesel environment at 800°C . (a) Unworn surface; (b) unworn surface after 30 min sputter; (c) transfer layer; (d) transfer layer after 30 min sputter.



manner. The addition of nickel and molybdenum appeared to improve the wear characteristics of the partially stabilized zirconia–TiC couple, but not those of the Si_3N_4 –TiC couple. Molybdenum was not detected on the surfaces of the TiC–Ni–Mo pins, however, probably due to its high volatility at the temperatures expected at the pin–disc interface. Since nickel transferred from the disc to the pins as shown for the case of the TiC pins, it is also not clear what role the addition of nickel to the pins played in the wear behaviour.

3.2. Discs

The results of the analysis of the discs are shown in Figs 4 to 11. Secondary electron micrographs and corresponding Auger elemental peak maps are given in Figs 4 to 7, while typical Auger spectra and elemental depth profiles taken on as well as away from the wear tracks are shown in Figs 8 to 11. The results displayed in Figs 4 to 7 were all taken at approximately the same sputter depth to facilitate comparison (sputter time \cong 10 to 15 min including 5 to 6 min to remove the silver coating). It was found during depth profiling, that the modified layers varied in thickness over the

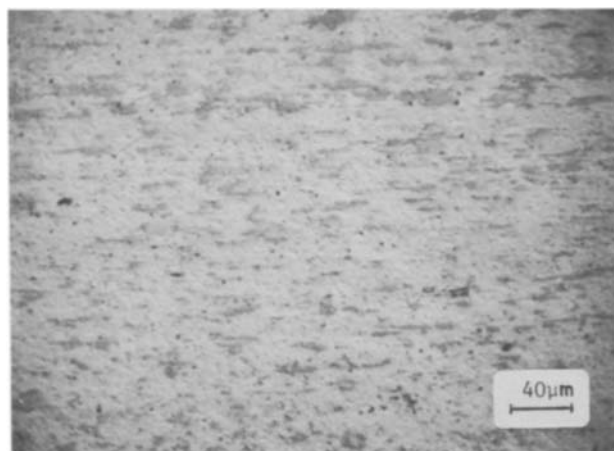


Figure 4 Wear track of Si_3N_4 (Ti, Ni) disc run against a TiC pin ($\mu_F = 0.09$) in a diesel environment at 800°C .

disc surfaces. Therefore, the profiles shown indicate the relative trends of elemental composition and depth, but no quantitative information is implied.

Elemental depth profiles of the discs as received after ion beam mixing are shown in Fig. 8. The layer is clearly not homogeneously mixed, with the components lying more or less as they were put down: substrate, nickel, titanium. The titanium layer was probably slightly oxidized during ion beam mixing, and some carbon, probably from specimen handling, has also been mixed in the outer layer. As previously mentioned, this may account for some of the carbon found in the transfer layers on the pins.

The morphology of the wear tracks is shown in the secondary electron micrographs of Figs 4 to 7. A comparison of Figs 4 and 5a for Si_3N_4 , and Figs 6a and 7 for the zirconia, indicate that the wear tracks of the low μ_F discs have a finer structure than those of the corresponding high μ_F discs. The mechanism of wear appears to be that of delamination as first suggested by Suh [15], where material is removed in thin sheets by a shear-type deformation. The delamination generally occurs at the modified layer–substrate interface, with the high μ_F discs showing a much larger degree of such delamination than the low μ_F discs. For the Si_3N_4 case, this can be seen in Figs 5b–d, where the flat regions, examples of which are indicated by the arrows, correspond to regions of silicon and lack of the modified layer as seen in the Auger peak maps. The low μ_F Si_3N_4 disc also shows a delamination type of wear, seen by streaks of silver left where laminates have shadowed the neighbouring region from the ion beam, Fig. 4, but little sign of the substrate was observed. Modified layer–substrate delamination is more obvious on the low μ_F zirconia disc, Fig. 6a–c, where arrows again indicate examples of where the substrate appears [Zr (147 eV) signal]. The high μ_F zirconia disc, however, clearly shows the greater degree of delamination, Fig. 7, where the dark laminates consist of titanium and nickel, and the light areas are zirconium oxide.

While quantitative depth analysis of these specimens

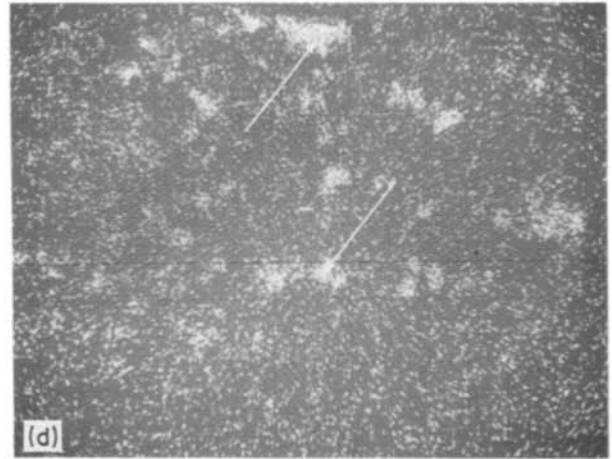
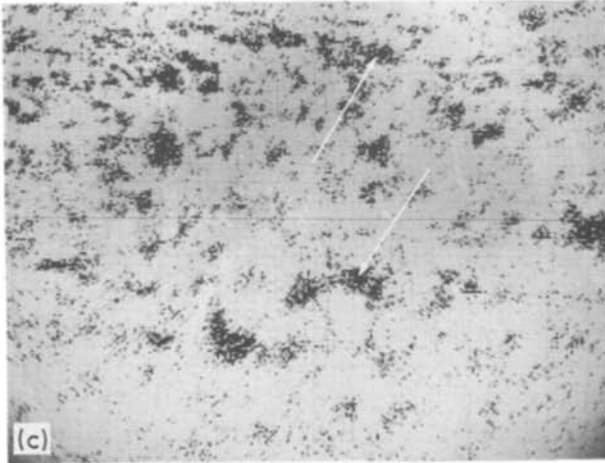
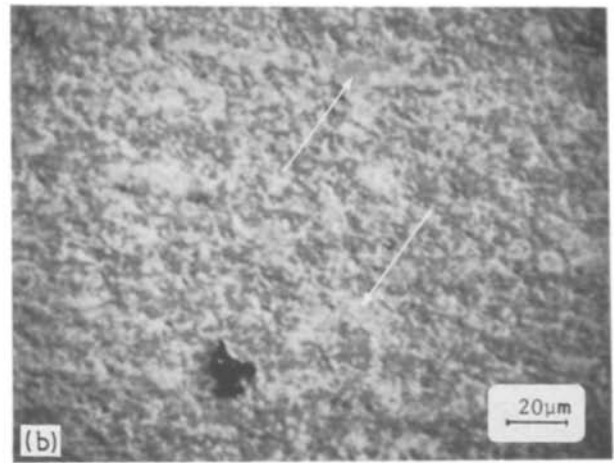
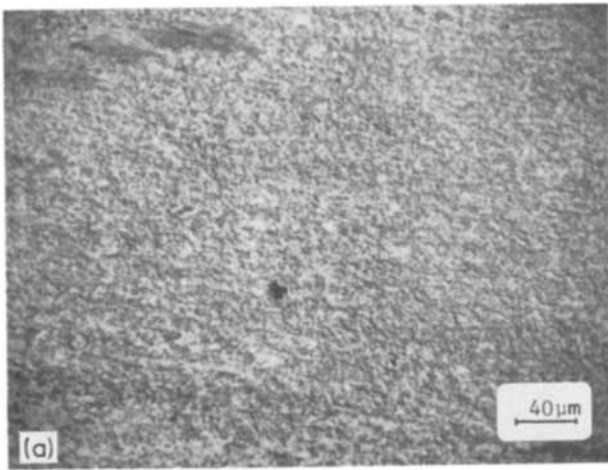
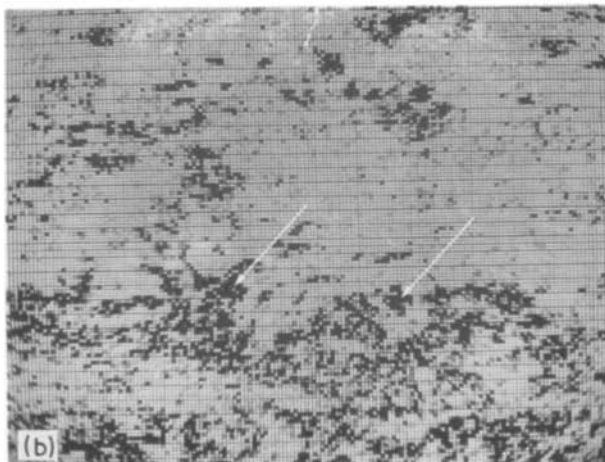
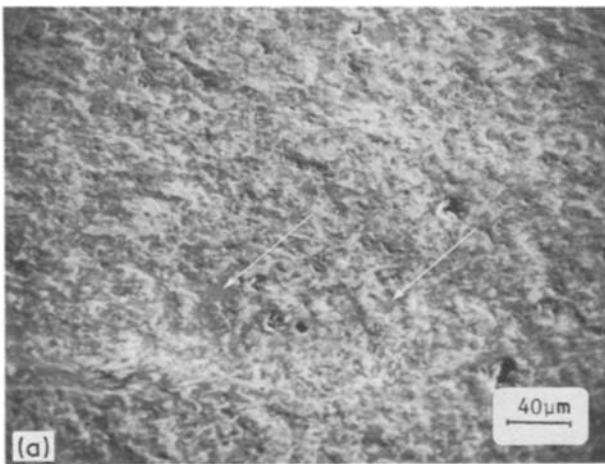
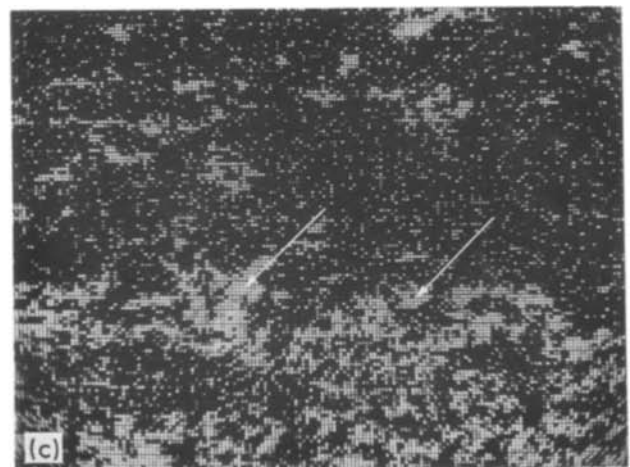


Figure 5 Wear track of Si_3N_4 (Ti, Ni) disc run against a TiC–Ni–Mo pin ($\mu_F = 0.22$) in a diesel environment at 800°C . (a and b) SEM micrographs; (c) Ti (387 eV) Auger map (cf. b); (d) Si (~ 83 eV) Auger map (cf. b).



is made difficult due to surface roughness and composition induced preferential sputtering, elemental depth profiling has provided useful qualitative information about the chemistry of the observed wear tracks. Elemental depth profiles taken at various points on and away from the wear tracks indicate that, under the temperature and/or pin pressure conditions of the tests, the composition profile of the modified layer had changed considerably during the tests from that of the as-received discs, Fig. 8.

Figure 6 Wear track of PSZ (Ti, Ni) disc run against a TiC–Ni–Mo pin ($\mu_F = 0.09$) in a diesel environment at 800°C . (a) SEM micrograph; (b) Ti (387 eV) Auger map; (c) Zr (147 eV) Auger map.



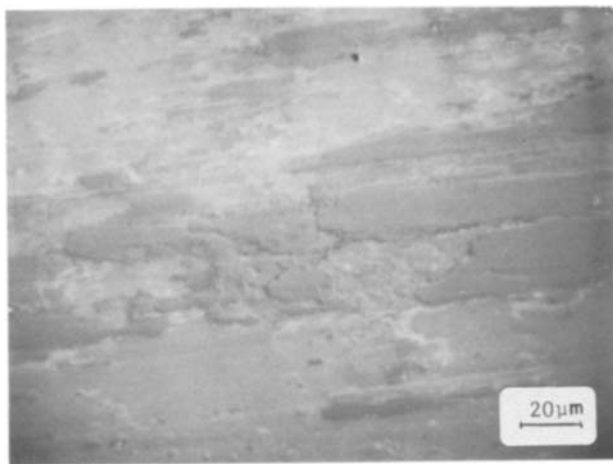


Figure 7 Wear track of PSZ (Ti, Ni) disc run against a TiC pin ($\mu_F = 0.25$) in a diesel environment at 800° C.

Typical depth profiles taken away from the wear track are shown in Fig. 9. In the case of the Si_3N_4 discs, Fig. 9a, it appears that the titanium layer has retained its profile while the nickel has diffused to the surface of the disc. While not obvious from the profiles themselves, examination of the individual spectra used to make up the silicon profiles indicate that silicon becomes detectable approximately half-way through the profile. The titanium profile has also been retained on the zirconia disc, Fig. 9b, but the layer is not as thick as that on the Si_3N_4 disc, nor is nickel present on the surface. Zirconium was not detectable until near the end of the modified layer. The modified layers on both types of discs were clearly oxidized under the test conditions. The shape of the oxygen profile follows that of the titanium layer and changes in the titanium Auger spectra were similar to those observed for the pins, as shown in Fig. 10. This does not, however preclude the fact that the nickel layer may also be oxidized, since the nickel profile was flat.

Nickel tends to vaporize fairly easily at high temperature. A loss of nickel at the surface of the disc would thus not be unexpected. However, the presence

of nickel on the surface of the Si_3N_4 disc, along with evidence of mixing of the substrate, indicates that the modified layer may be better bound to Si_3N_4 than to zirconia. This could also be concluded from the SEM observations, where both the low and high μ_F zirconia discs exhibit more exposed substrate than the corresponding Si_3N_4 discs.

A typical elemental depth profile from the implanted layer left on the wear track is shown in Fig. 11. This example from a Si_3N_4 disc shows a small amount of nickel at the surface followed by the titanium layer mixed with nickel. This is in contrast to the unworn areas which showed a thicker surface nickel layer as measured by sputter time. Slight variations in the thickness of the surface nickel layer on the wear tracks were noted depending on how high or low a particular lamination was situated relative to its surroundings. The laminates left on the zirconia disc wear tracks showed virtually no surface nickel. The pins run against them did, however, show a large amount of nickel. Analogous to the case of the unworn areas, it is possible that nickel diffused to the surface of the discs and then transferred to the pins. The fact that some nickel remained on the surface of the Si_3N_4 discs and not the zirconia discs, again indicates that the implant layer may be better bonded to Si_3N_4 .

The thickness of the laminates could not be determined because of surface roughness effects on sputtering. Low regions, especially any exposed substrate, tended to be preferentially sputtered, making the laminates appear very thick. Assuming that nickel was removed from the surface (and possibly deposited on the pins), it would be logical to assume that the laminates would be thinner than the original implant layer. It is also possible, however, that material could have piled up locally on the wear track. The pin would then be riding on this raised lamination layer. This does not seem as likely since a pile-up would be indicated by a significant compositional change in the depth profiles, rather than just the removal of surface nickel.

Further evidence for the better mixing of the modified layer on Si_3N_4 rather than zirconia was obtained

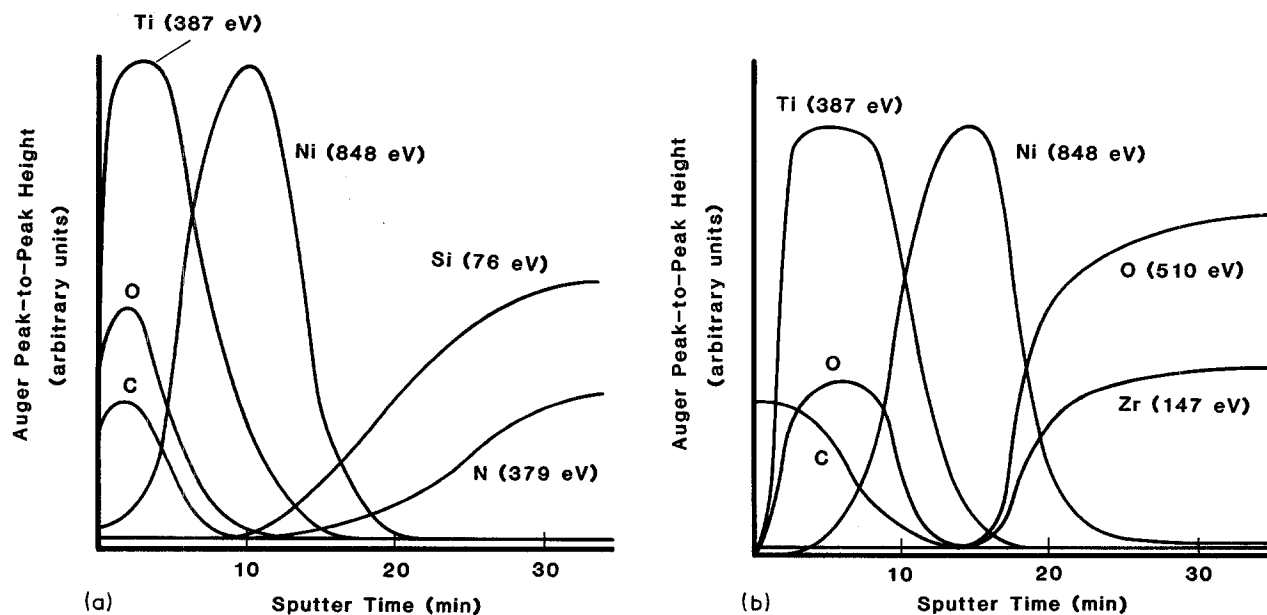
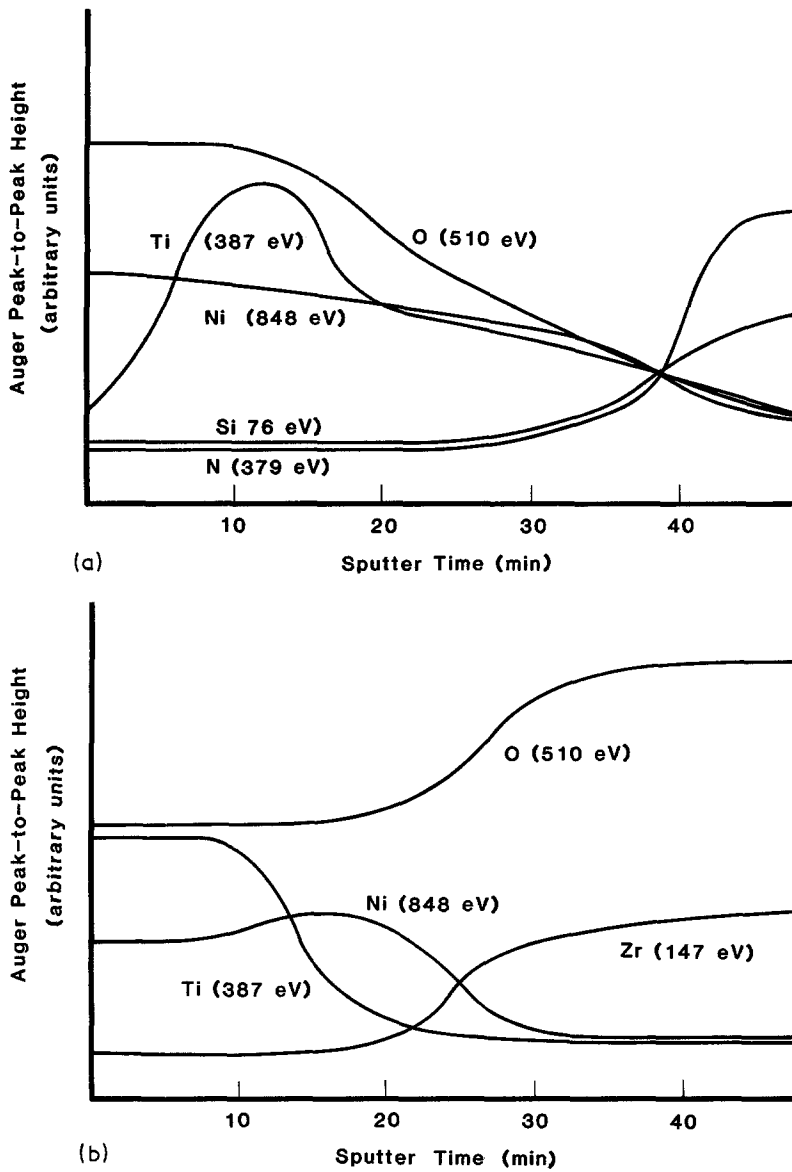


Figure 8 Elemental depth profiles of ion beam modified discs before testing. (a) Si_3N_4 (Ti, Ni); (b) partially stabilized zirconia (Ti, Ni).

Figure 9 Elemental depth profiles taken away from the wear track. (a) Si_3N_4 (Ti, Ni); (b) partially stabilized zirconia (Ti, Ni).



from analysis of the delaminated regions of the wear track. A thin layer of nickel generally covered these regions, although the substrate signal appeared fairly strong. Upon sputtering, however, the nickel signal disappeared fairly rapidly from the zirconia discs while it remained for some time on the Si_3N_4 discs.

4. Discussion

The results of this preliminary surface investigation into the wear of ion-beam modified ceramic discs indicate that several factors may govern the wear properties of these materials in the high temperature environment used. These include the adhesion of the

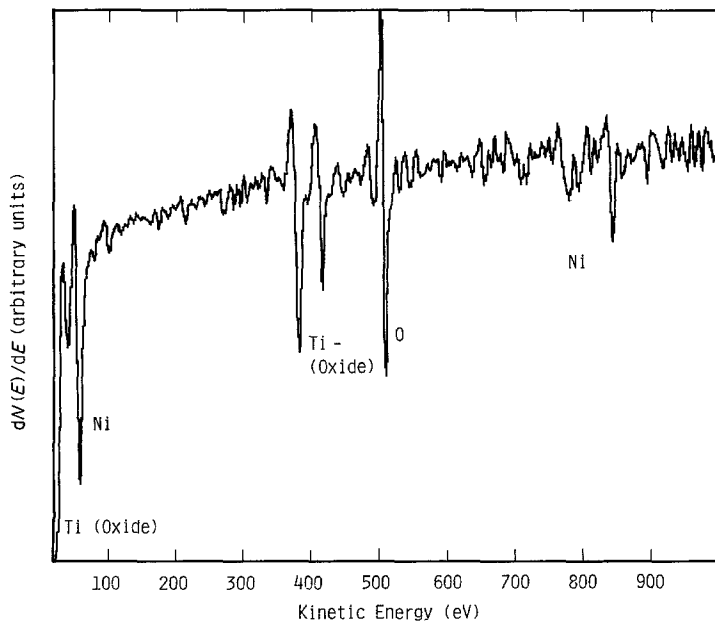


Figure 10 Typical Auger spectrum taken after partial sputter removal of the (Ti, Ni) layer from a disc. Note the evidence for titanium oxide (40 eV peak, peak height ratio $\text{Ti}_{387}/\text{Ti}_{418} > 1$).

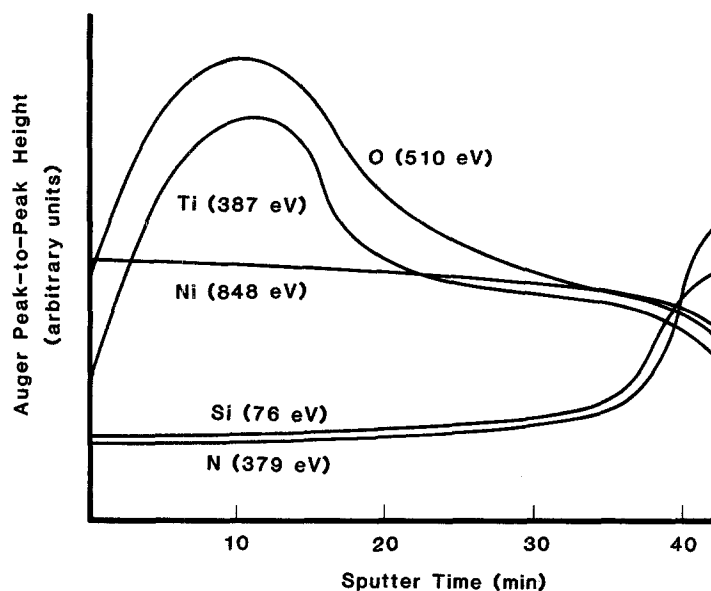


Figure 11 Elemental depth profile of an ion beam mixed layer laminate left on the wear track of a Si_3N_4 disc.

modified layer to the ceramic, the transfer of material between the surfaces of the pins and discs, and the chemical state of the surface material (oxide) and the pin material.

The adhesion at the modified layer–ceramic boundary is clearly important in a delamination type of wear since this would be the weakest interface. Both the micrographs and depth profiles indicate that the TiNi layer adhered better to the Si_3N_4 than the zirconia in the low as well as the high μ_F cases. However, even on the low μ_F Si_3N_4 disc, small amounts of relatively bare substrate were occasionally detected, thus raising the possibility that a longer term test would result in the eventual removal of the modified layer on all of the discs. The wear resistance of the layer on Si_3N_4 would then be of only temporary benefit. Long term tests (> 1 h) are now under way to examine this point. It may be noted here that ion beam mixing of chromium produced no beneficial effects in either disc material. On the contrary, it was almost completely worn off, leaving virtually no trace on the wear track, thus indicating poor adhesion to the substrate.

The transfer of material, or the formation of a surface oxide, has been shown to be beneficial to the wear characteristics of many systems [16, 17]. In the present case, nickel appears to have been transferred from the discs to the pins. It was obviously not possible to determine whether or not titanium transferred to the pins; a radioactive tracer technique would be useful in this case. There is no doubt, however, that the titanium present in both the pins and the implant layer has been oxidized. It is not clear whether one or both processes, nickel transfer and/or modified layer oxidation, are required to improve wear characteristics. Wear tests run at high temperature in argon [1] showed poorer wear characteristics than in the oxygen containing diesel environments, even though material transfer took place. However, as will be discussed shortly, TiC and TiC–Mo–Ni pins run against uncoated ceramic discs showed better wear characteristics than other pin materials due to the transfer and oxidation of titanium from the pins to the discs.

Related to the material transfer question is the

choice of pin material. For the present four pin disc combinations, the pin material played a confusing role. Nickel was clearly transferred to all four pins, but the two pin materials had opposite effects with respect to disc material in couples 1 to 4. Molybdenum was not detected on any of the wear surfaces of couples 2 and 4. This would be expected due to the volatility of molybdenum at the high temperatures expected at the contact point. The role of pin material is at the moment not understood. However, the choice of pin material has played a major role in other pin–disc systems. TiC or TiC–Ni–Mo pins have produced lower coefficients of friction than silicon carbide (SiC) pins when run against uncoated Si_3N_4 , zirconia and chromium surface modified Si_3N_4 and zirconia discs. This may be due to the fact that titanium transferred from the pins to the discs, while silicon did not (as observed using energy dispersive spectroscopy, EDS).

5. Conclusions

A preliminary surface study has been performed with scanning Auger electron microscopy to examine the wear of ion beam modified ceramic materials to be used in high temperature adiabatic engines. The wear surfaces of pin–disc combinations showing promising wear properties in terms of low coefficients of friction and weight loss, were examined and compared with those showing less promising wear properties. Of all pin–disc combinations tested, TiC or TiC–Ni–Mo pins run against Si_3N_4 or zirconia discs surface ion beam mixed with a double layer of titanium and nickel showed the best wear properties. There were significant differences among these combinations, however, which indicate that several factors play an important role in the wear process. These include:

- (i) the transfer of material between members of a wear couple;
- (ii) the formation of a possibly lubricating oxide layer;
- (iii) the choice of pin material;
- (iv) in the case of the surface treatment of ceramic wear parts such as with ion beam mixing, the adhesion properties of the modified surface layer.

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