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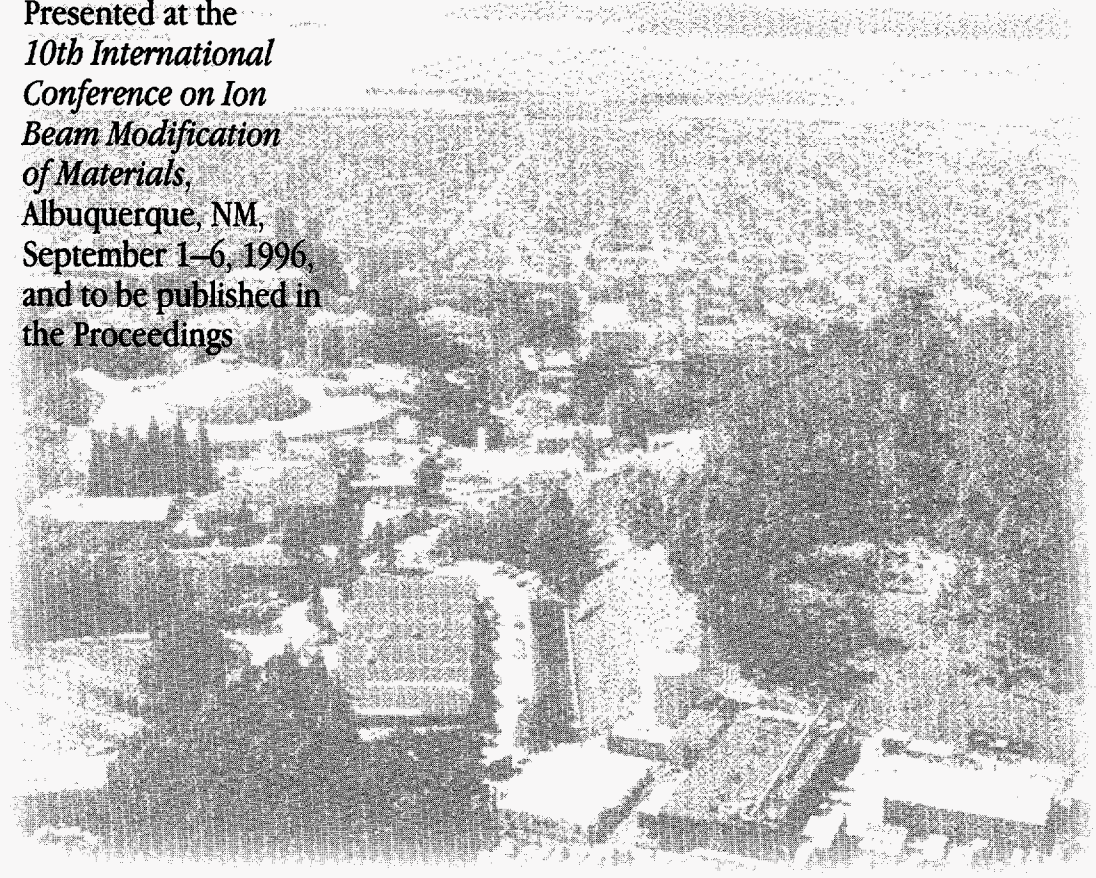BERKELEY LAB

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WITH A MODIFIED VACUUM ARC ION SOURCE

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Abstract

Energetic beams of mixed metal and gaseous ion species can be generated with a vacuum arc ion source by the addition of gas to the arc discharge region under appropriate conditions. This operational mode could prove to be an important tool for ion implantation research by providing a method for forming buried layers of mixed composition such as, for example, metal oxides and nitrides. In work to-date, we have formed a number of mixed metal-gas ion beams including Ti+N, Pt+N, Al+O and Zr+O. The particle current fractions of the metal-gas ion components in the beam ranged from 100% metallic to approximately 80% gaseous depending on the operational parameters. We have used this new variant of the vacuum arc ion source to carry out some exploratory investigations of the effect of Al+O and Zr+O co-implantation on the tribological characteristics of stainless steel. Here we describe the ion source modifications, the species and charge state composition of the hybrid beams produced, and the results of some preliminary investigations of the surface modification of stainless steel by co-implantation of mixed aluminum / oxygen or zirconium / oxygen ion beams.

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1. Introduction

Operation of ion sources with mixed metal-gas species has been mostly confined to relatively low beam current such as can be produced for example by PIG [1] or Freeman sources [2]. High-current broad-beam ion sources that are of potential application for large scale non-semiconductor surface modification have been operated as purely gaseous or purely metallic ion beam generators, for example magnetic bucket sources of various embodiments [3,4] and vacuum arc ion sources [4-6]. On the other hand, it is sometimes desirable for metallurgical and other surface modification applications to form buried layers of mixed metal-gas species. One way of doing this that has been employed with success is to use an ion mixing approach in which one species (the condensible species, ie, the metal) is deposited on the surface by a low energy process such as evaporation or sputtering, and the second species (the gas) is energetically directed to the substrate. Then the gas species is implanted in the usual way while the metal species is also 'recoil implanted' by knock-on collisions with energetic gas ions [7].

There could be advantage in an approach in which both the metal and gas ion species are implanted energetically at the same time. Although this mode of operation is clearly a possibility if two independent ion sources are used, the expense and system complexity of this way of operating are daunting. Production of both metal and gas species by a single ion source would be attractive.

We have developed a modification to the vacuum arc ion source in which hybrid metal-gas ion beams are formed and by means of which co-implantation of energetic metal and gaseous species can be carried out. The vacuum arc ion source is essentially a metal ion source, but when gas is added to the arc region in the presence of a magnetic field, ionization of the gas can occur within the metal plasma and energetic beams of mixed gaseous and metallic species can be produced. The effect of gas on the arc plasma development has been investigated by several workers [8-10], and

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operation of a vacuum arc ion source at elevated background gas pressures has been reported previously [11,12]. Related work on the production of gaseous ion species in vacuum arc ion sources has been carried out at GSI (Darmstadt) [13,14], and co-implantation of metal/gas species has been demonstrated by workers at Tomsk [15]. Here we outline the ion source innovations made and beam performance obtained by us, and summarize the results of some fundamental investigations we've carried out using the method for the surface modification of stainless steel by co-implanting (i) mixed aluminum and oxygen, and (ii) mixed zirconium and oxygen.

2. Experimental

For the work described here, an LBNL multi-cathode, broad-beam, vacuum arc ion source was modified by the addition of a small, pulsed magnetic field coil to the arc region of the source [16,17]. Gas is then fed to the cathode-anode region in the presence of a magnetic field of strength about 2 - 3 kG; we have used primarily oxygen and nitrogen to-date. Typically the vacuum arc is pulsed to ~200 A for a pulse length of ~250 μs at a repetition rate of ~10 pps. Beam is formed by the 10-cm diameter extraction electrodes at a voltage of typically 50 kV, and an ion current of several hundred mA is detected by a radially-moveable, 5-cm diameter, magnetically suppressed, Faraday cup located about 65 cm downstream from the source. The target specimen to be implanted is introduced into the beam by a target holder, which can also be moved radially, located adjacent to the Faraday cup. The ion beam charge state distribution is measured by a time-of-flight system [18]. Background gas pressure is in the 10^{-6} to 10^{-4} Torr range depending on the gas flow rate at the ion source. All details of the ion source operation and the experimental set-up have been described in more detail elsewhere [6,19].

We performed two different implantation experiments using this experimental set-up. In the first experiment we implanted a series of polished type-304L stainless steel disks with Al+O to a dose of about 1×10^{17} cm^{-2} (total Al + O) for a range of different Al:O ratios; the mean Al ion energy

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was about 85 keV and the mean O energy about 34 keV. Wear and friction measurements were made on the disks. The central portion (about 16 mm diam.) was masked during implantation to preserve a reference surface. A pin-on-disk tribometer (CSEM) fitted with a ruby ball (6 mm diam.) was used for these measurements which were carried out under a load of 2 N and at a constant speed of 0.02 m/s. Both dry and lubricated (flowing ethanol) conditions were investigated; the former provided a convenient means of determining the effect of implantation on the coefficient of friction, while the latter was used to monitor changes in surface hardness. The resulting wear track profiles were recorded by means of a profilometer (Tencor Instruments) which also has a facility for estimating the cross-sectional area of the track. In the second experiment we implanted a number of stainless steel (type 316L) test plates and rods with Zr+O to a dose of about 1×10^{17} cm^{-2} (total Zr + O). X-ray diffraction analysis was carried out on the implanted samples, and measurements of friction, wear and microhardness were made.

3. Results

3.1 Structure of the hybrid beam

The precise dependence of the beam metal/gas ion mix and charge state composition as a function of gas pressure depends parametrically on the value of magnetic field at which the pulsed field coil is driven; the data presented here are typical. Results for the case of a mixed Al+O ion beam are shown in Figure 1. The fraction of Al ions (total Al^+, Al^{2+} and Al^{3+}) and O ions in the beam (total O_2^+ and O^+) are plotted as a function of system pressure. Similar behavior is seen also for Ti+N and Zr+O beams. The gaseous ion fraction can be greater than the metal ion fraction, and a 40:60 Al:O atomic ratio (as in Al_2O_3) is obtained at a pressure of 9.6×10^{-5} Torr. For molecular gases like oxygen or nitrogen, both molecular and atomic ions are observed, and their relative proportions are dependent on magnetic field as well as gas pressure; the atomic ion fraction increases and the molecular component decreases with decreasing gas pressure and with increasing magnetic field strength. The charge state multiplicity of the metal ions decreases as the gas

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pressure is increased; the low charge state fractions are increased and the high charge state fractions decreased. Figure 2 shows the measured mean ion charge state as a function of system pressure. At 9.6×10^{-5} Torr operating pressure the Al ion beam is 40% Al^+, 50% Al^{2+} and 10% Al^{3+}, for a mean charge state of 1.7; and the O ion beam is 65% O_2^+ and 35% O^+, for a mean charge state of 0.67 (ie, primarily molecular ions). Note that throughout this paper we refer to ion current and ion fractions with respect to particle current i_p, not electrical current i_e; $i_p = i_e/Q$.

3.2 Co-implantation depth profiles

The beam is highly structured, with three different Al energy components and two different O energy components. For an extraction voltage of 50 kV, the Al ion beam contains 40% of ions at energy 50 keV, 50% at 100 keV and 10% at 150 keV, for a mean Al ion energy of 85 keV. The O ion beam contains 65% of ions at energy 25 keV (ie, "half-energy" due to the O_2^+ molecular ion) and 35% at 50 keV, for a mean O ion energy of 34 keV. The total beam is then composed of 40% Al ions and 60% O ions (counting the molecular O_2^+ as two ions at half-energy). The ranges of the metal and gaseous species in the substrate material may be different, with the actual implantation depths depending not only on the ion charge state and energy but also on the substrate material and particularly on the incident metal and gaseous ion masses. Figure 3 shows the results of TRIM depth profile calculations [20,21] (we used TRIM-92) for the case of Al and O implanted into stainless steel at the above energies. We used the actual measured Al and O ion beam energy (charge state) distributions as just described, and the Al and O profiles are the sums, appropriately weighted, of implantations of the various energy beam components. The net effect of the beam energy structure is to broaden the depth profiles and enhance the overlap of the implanted metal and gas species. For the Al+O implantation investigated here, the implantation depth is roughly 350 Å with half-concentration points at about 150 and 750 Å. The 2:3 Al_2O_3 atomic ratio cannot be maintained everywhere throughout the profile because the Al and O depth profiles are not the same shape. But it's clear that the overall co-implantation depth profiles are very suitable for the present purposes.

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3.3 Co-implantation experiments

Typical wear track profiles for the unimplanted and the 50:50 Al+O implanted stainless steel (type 304L) are shown in Figure 4. A significant reduction in wear is clearly evident following implantation. Multiple profilometer scans across these tracks yielded average cross-sectional areas of 28.0 and 2.9 for the unimplanted and the implanted regions respectively. This represents an improvement by a factor of about 10. The implantation of Al+O also produced a marked effect on friction as can be seen from the data presented in Figure 5. In each case the test was of 100 revolutions duration under dry conditions with a 2 N load and a constant linear velocity of 0.02 m/s. The coefficient of friction of the modified surface was substantially lower by factors which ranged from ~4 at the beginning of the run to ~2 at its completion. It is thus clear that co-implantation of Al+O into type-304 stainless steel yielded a significant reduction in both wear and friction.

In the second experiment we implanted a number of stainless steel (type 316L) test plates and rods with Zr+O to a dose of about 1×10^{17} cm^{-2} (total Zr + O). The post-implantation samples had a beautiful, shiny, deep steel blue color. Measurements of friction, wear and micro-hardness indicate that the coefficient of friction decreased by a factor of six, from 0.6 to 0.1; that the wear volume of implanted samples decreased by about 5.5 times; and that the micro-hardness increased by 60%, from 3 GPa to 5 GPa. X-ray diffraction showed that the surface has an amorphous structure.

4. Conclusion

High current beams of mixed metal and gas ion species have been formed using a modified broad-beam vacuum arc ion source. Hybrid Al+O and Zr+O ion beams were produced and characterized as a function of source parameters; metal-to-gas ratios equal to those in the stoichiometric oxide materials can readily be obtained. Co-implantation of Al+O and of Zr+O into stainless steel

samples was carried out and the specimens evaluated for wear, hardness, and friction. Significant improvements in all of these parameters were observed: the wear decreased by up to a factor of from 5 to 10, the microhardness increased by about 60%, and friction decreased by a factor of from 2 to 4.

Acknowledgements

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Figure Captions

Fig. 1   Fraction of Al ions (total Al^+, Al^{2+} and Al^{3+}) and O ions (total O_2^+ and O^+) in the beam as a function of system pressure.

Fig. 2   Mean Al and O ion charge states as a function of system pressure.

Fig. 3   TRIM-calculated ion depth profiles for Al (with a 40% 50keV, 50% 100 keV and 10% 150 keV energy structure) and O (with a 65% 25 keV and 35% 50 keV energy structure), and with an Al:O ratio of 2:3, into stainless steel (Fe:Ni:Cr = 74:18:8).

Fig. 4   Profilometer scans of pin-on-disc wear tracks on unimplanted (broken line) and Al+O implanted (solid line) regions of type 304L stainless steel specimen. Test conditions were: load, 2N; velocity, 0.02 m/s; total revolutions, 1000; lubricant, ethanol.

Fig. 5   Friction records of pin-on-disc tests on unimplanted (upper trace) and Al+O implanted (lower trace) regions of type 304L stainless steel specimen. The total length of the non-zero portion of each trace corresponds to 100 revolutions. Other test conditions were: load, 2N; velocity, 0.02 m/s; no lubricant.
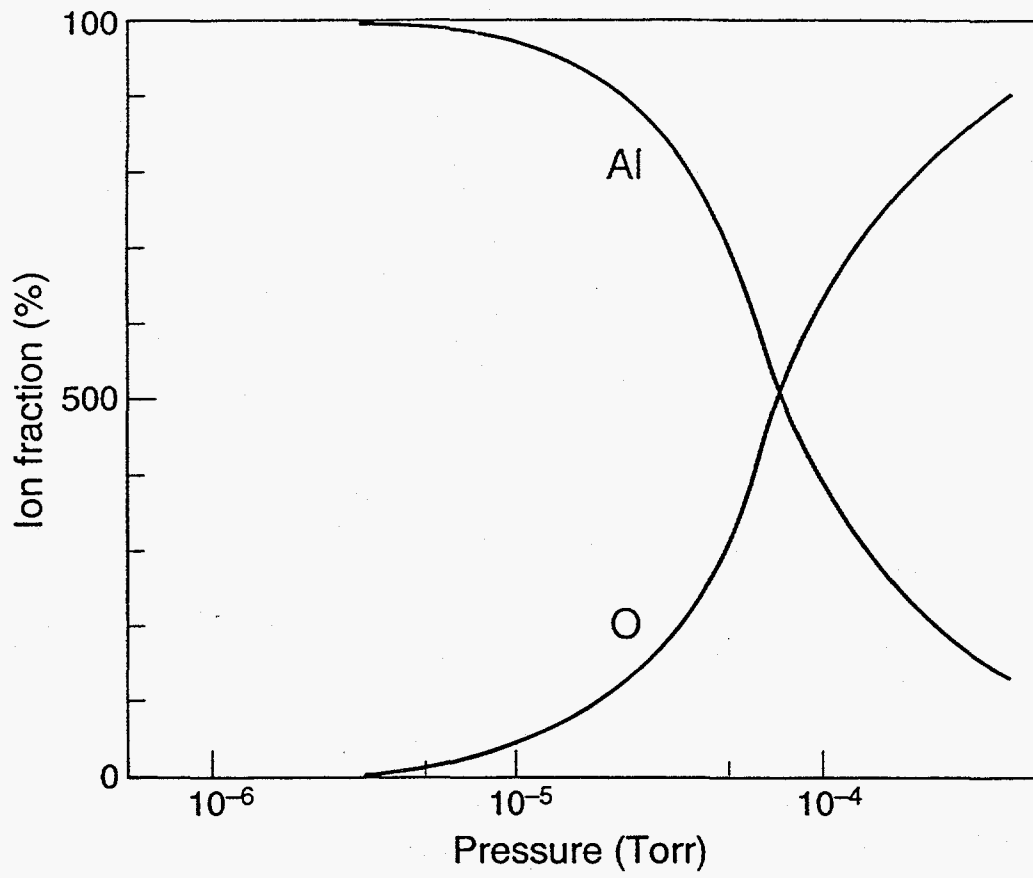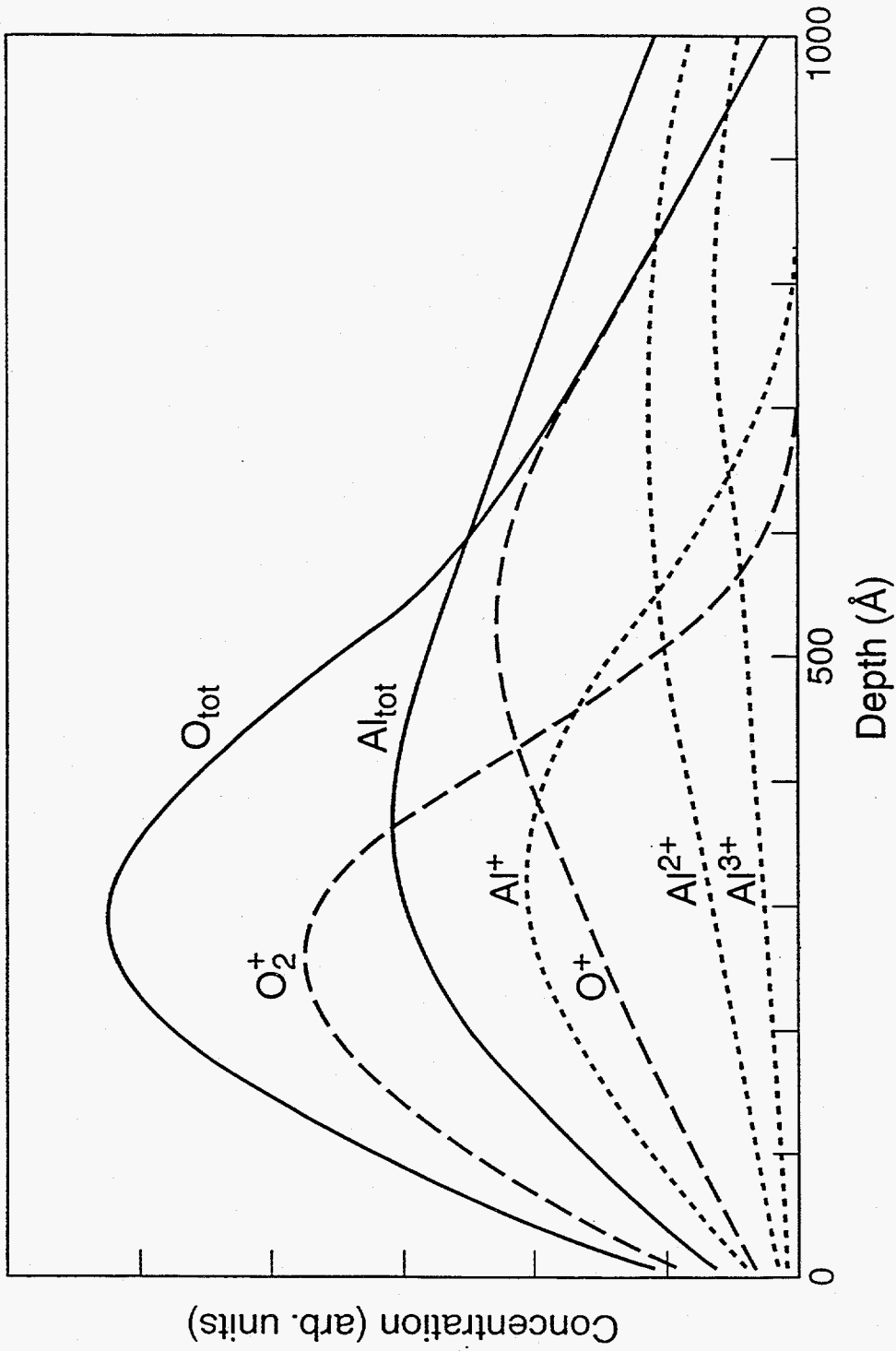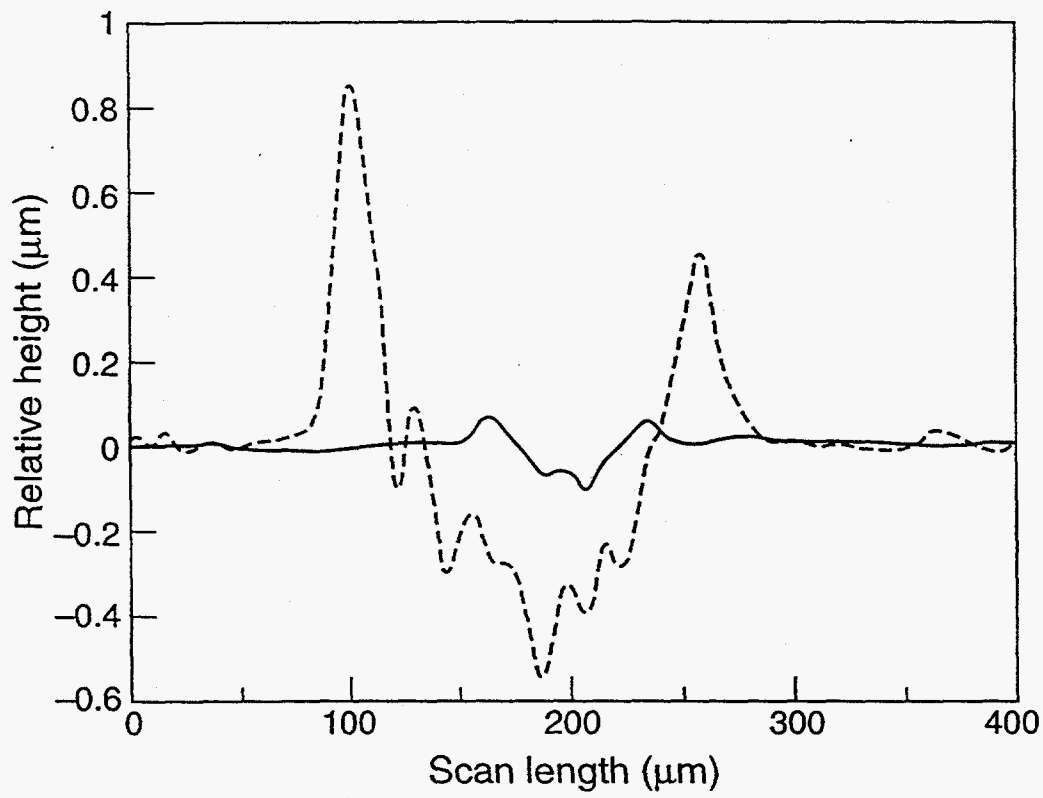
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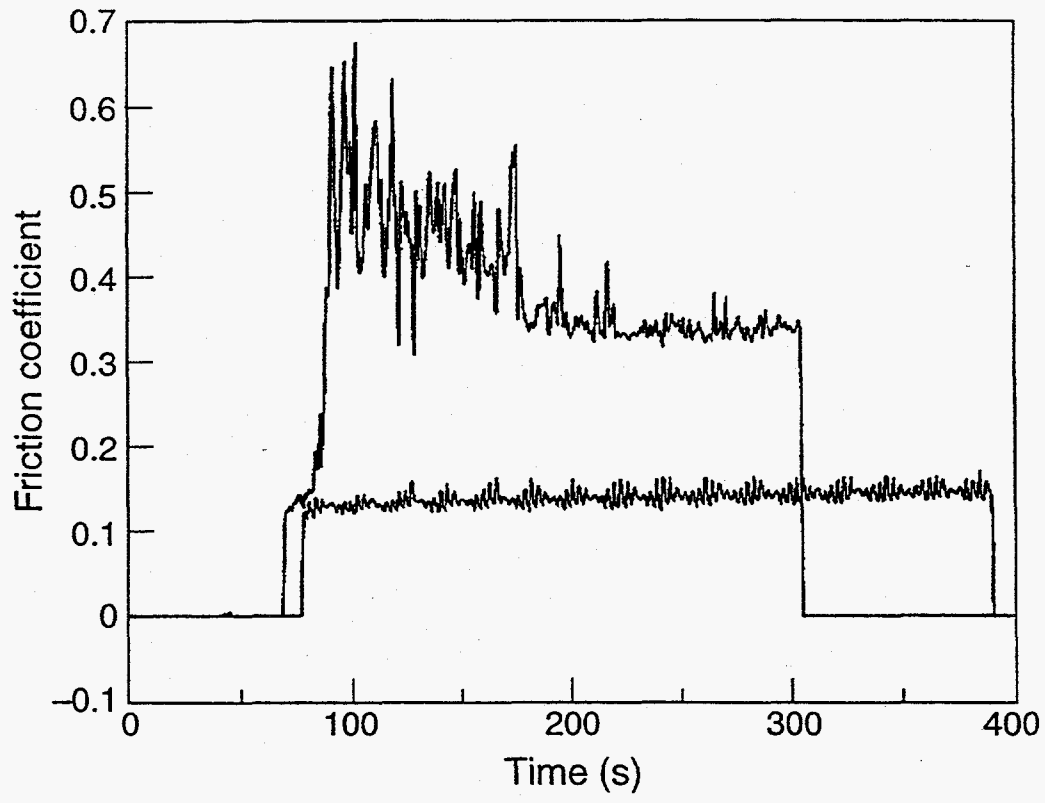Figure 1
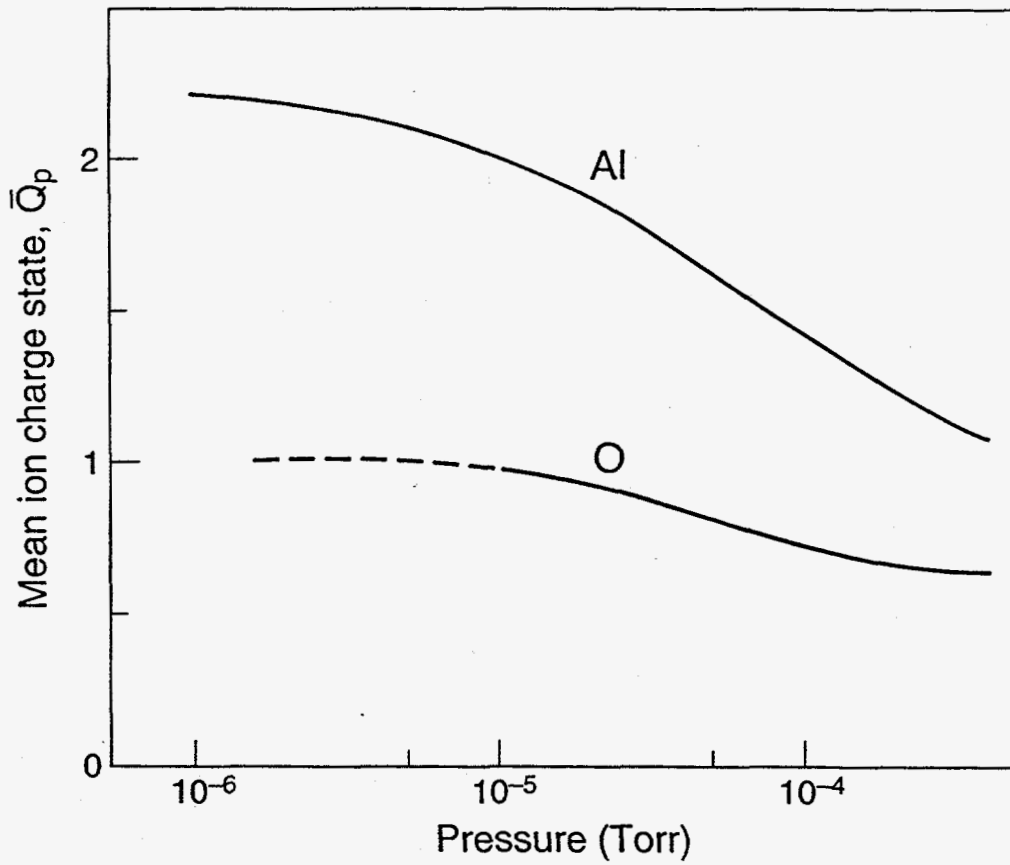
Figure 2

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Figure 3

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Figure 4

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Figure 5

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