Emission of neutral Mg from single crystal MgO during abrasion with diamond

Myoung-Won Kim, S. C. Langford, and J. T. Dickinson[a)]
Department of Physics, Washington State University, Pullman, Washington 99164-2814

(Received 11 July 2002; accepted 1 November 2002)

We report observations of atomic, neutral Mg emitted from single crystal MgO during abrasion with a diamond stylus. These emissions take the form of bursts, where the onset of each burst coincides with a slip event often associated with the passage of the stylus over a cleavage step. After the onset, the emission intensity grows gradually to a peak, then drops sharply. Similar bursts of neutral Mg are observed when indented single crystal MgO is heated to temperatures above 1300 °C. We attribute these bursts to the emission of neutral Mg during the relaxation of dislocation-related structures produced by mechanical deformation. Strain energy released as these structures annihilate at the surface drive Mg emission and heat the surrounding material. This heating accelerates subsequent relaxation, increasing the emission intensity until relaxation is complete and the emission rate drops sharply. © *2003 American Institute of Physics.* [DOI: 10.1063/1.1532937]

I. INTRODUCTION

Substrate damage during abrasion and wear of brittle materials can involve extensive deformation and fracture. In vacuum, both of these processes are often associated with the emission of photons and particles, including electrons, positive ions, and neutral molecules. These emissions constitute so-called ''fracto-emission,'' which is reviewed in Refs. 1–4. In the case of MgO, deformation and fracture produce intense photon emission[5,6] and electron emission.[6] Both signals can be measured in a time-resolved fashion during wear.[7] These emissions are strongly correlated with individual fracture and deformation events and can be used to distinguish between them.

Neutral particles are emitted during and after fracture of many brittle and semibrittle materials, including alkali halides,[8] semiconductors,[9] and silicate glasses.[10] Significantly, neutral emissions from the alkali halides and germanium take the form of sharp bursts many milliseconds after the fracture event. These emissions are attributed to the relaxation of dislocation structures produced during fracture.[8,9] Localized relaxation can deposit sufficient energy near the surface to stimulate particle emission. Comparable bursts of CO_2 are observed following the fracture of calcium carbonate (calcite)[11] and are attributed to localized decomposition. In the case of MgO, fracture yields several neutral species,[12,13] including atomic and molecular oxygen, CO_2, and atomic Mg; the time behavior of neutral Mg in particular is unique among the fracture-induced emissions reported to date.[12] Weak Mg emission typically begins immediately after fracture, grows to a peak over some milliseconds, then falls dramatically. This behavior is typical of an autocatalytic process, where the reaction rate increases dramatically until the reactants are consumed.

The emission of neutral atoms and molecules during abrasion is less well studied. Bursts of CO_2 are observed during the abrasion of single crystal calcite.[14] Similar bursts of Na and NO are observed during the abrasion of single crystal $NaNO_3$.[14] In both cases, the bursts are attributed to anion decomposition that accompanies localized relaxation of deformation structures.

In the present work, we focus on the emission of atomic Mg during the abrasion of single crystal MgO with diamond. Simultaneous lateral force measurements indicate that neutral emissions begin immediately after a slip event, often when the diamond stylus passes over a cleavage step. Like the fracture-related emissions, they grow to a peak many milliseconds later, then fall sharply. Neutral emission measurements during the rapid heating of highly deformed, single crystal MgO in vacuum show similar behavior, beginning at temperatures at which dislocation mobility becomes significant. Thus the neutral Mg emission during heating appears to be associated with the relaxation of deformation-related structures, such as dislocations or slip bands. We attribute the bursts observed during abrasion to the relaxation of similar structures produced during abrasion.

II. EXPERIMENT

Single crystal MgO substrates ($2\times2\times0.3$ cm^3) were cleaved from single crystal material from Tateho Chemical Industries, Ltd. Cleavage was performed on a stainless steel anvil by aligning a razor blade along a {001} cleavage plane and gently tapping the blade with a small hammer. The resulting surfaces displayed large numbers of cleavage steps. To provide smoother surfaces for testing, some samples were polished to a 0.25 μm finish with diamond paste.

A diagram of the abrasion experiment appears in Fig. 1. Abrasion was performed with a natural diamond obtained from Ward's Scientific (the radius of curvature of the contact was $\sim$500 μm) that was mounted rigidly at the end of a stainless steel cantilever. By moving the sample mount at

a)Author to whom correspondence should be addressed: electronic mail: jtd@wsu.edu

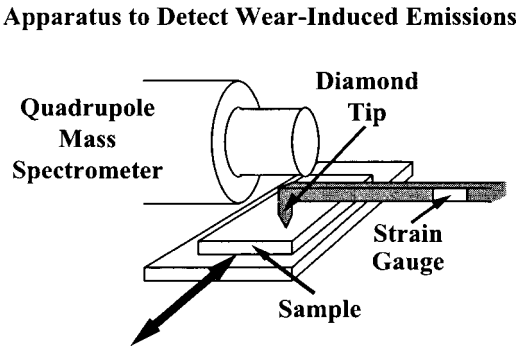

FIG. 1. Diagram of the abrasion experiment.

constant velocity (maximum 1–2 cm/s), abrasion could be performed without moving the point of diamond/sample contact relative to the detector. This arrangement allows high, constant efficiency for particle detection throughout the experiment. All of the time-resolved measurements described below involved single passes of the diamond over fresh, previously untested portions of the surface. A normal force of approximately 35 N was applied to the diamond.

Experiments were performed in vacuum with a background pressure of 10^{-7} Pa. Neutral emissions were detected with a UTI 100C quadrupole mass spectrometer, mounted with the ionizer about 1 cm from the center of the wear track. Neutral particles entering the ionizer were ionized by electron impact (70 eV electron energy). After passing through the mass filter, the ions were detected with a Channeltron electron multiplier. The Channeltron output was amplified with the internal electrometer of the UTI 100C and digitized with a LeCroy 6810 digital wave form analyzer.

The lateral force applied to the diamond stylus was measured with foil strain gauges mounted on the stainless steel cantilever. The output of the strain gauge resistance network (190 μV/N) was amplified with a dc differential amplifier and digitized with a LeCroy 6810 digital wave form analyzer.

Emission measurements were also made during the heating of highly deformed MgO in vacuum in a tantalum resistance heater. Deformation was accomplished by forming an array of Vickers indents with loads up to 2 kg. To account for the contribution of volatile species from the heater itself and from nearby vacuum parts, the signal detected in an identical heating run without a sample in the heater was subtracted from the signal detected with a sample in the heater. Signals detected without a sample were virtually identical to signals detected with annealed MgO in the heater. Annealing removes much of the deformation-induced damage and eliminates subsequent Mg emission at the level of sensitivity attained in this work. The heater temperature was monitored by digitizing the output of a Chromel–Alumel thermocouple spot welded to the bottom of the heater at a single point. Due to differences in temperature between the heater and the sample, the thermocouple output represents an upper bound on the sample temperature.

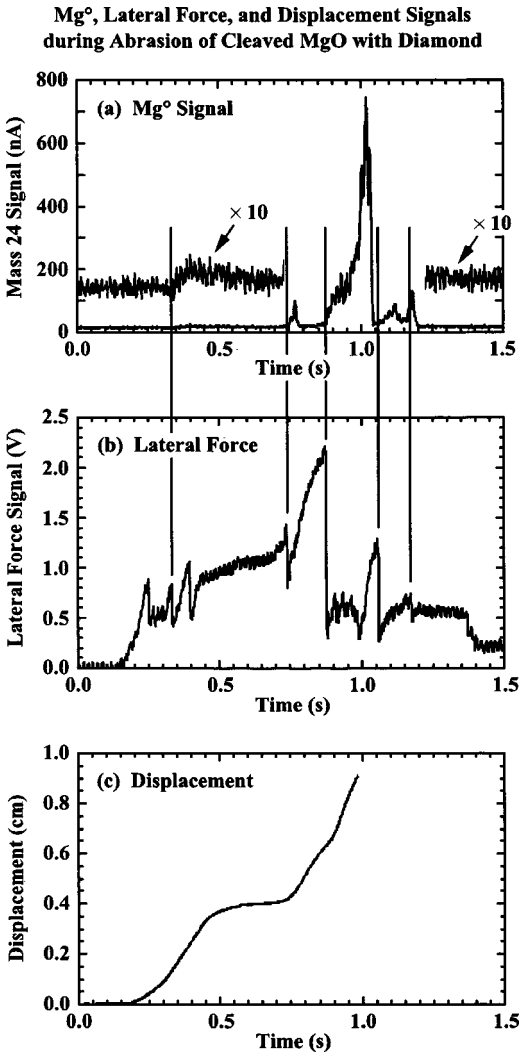

FIG. 2. (a) Neutral Mg, (b) lateral force, and (c) displacement signals during a single pass of a diamond tip across a cleaved MgO surface.

III. RESULTS

A. Mg emission during abrasion

Typical Mg, lateral force, and displacement signals during the abrasion of a cleaved MgO sample with a diamond stylus at a normal force of 35 N appear in Fig. 2. The stylus was drawn across the sample once only, reaching a maximum velocity of about 10 mm/s. Several Mg spikes appeared during this pass, and the *onset* of emission in each case is correlated with a drop in lateral force. Significantly, emission after a slip event tended to be initially rather weak, building up to a peak only after some tens or hundreds of milliseconds. The time of flight of Mg atoms and/or vacuum system response to this ''spray'' of Mg atoms are not issues here. The 100–200 μs time of flight of room temperature Mg from the sample to the detector is virtually instantaneous on this time scale. Placing a beam block between the sample and the ionizer completely eliminated the Mg signal at our level of sensitivity, confirming that Mg atoms bouncing off the vacuum system walls (if any) do not contribute significantly to the signals observed. Thus the observed signal is due to Mg atoms passing straight from the sample to the quadrupole

ionizer. Most emission events show a quasiexponential rise in emission intensity, followed by a dramatic drop. This behavior is characteristic of autocatalytic processes, where the reaction rate increases rapidly as the reaction proceeds. Here we expect the increasing emission reflects localized heating and not catalytic effects per se. Similar behavior was observed in Mg emission that accompanied fracture of single crystal MgO in three point bend.[12] This autocatalytic-like behavior contrasts markedly with the temporal evolution of other fracture-related emissions from MgO, which peak immediately after fracture and subsequently decay.[12] Neutral emission measurements during the fracture of many other inorganic materials yielded no other examples of autocatalytic-like behavior.[8,9,11,15]

Although every Mg burst in Fig. 2 is associated with a drop in lateral force, several drops in lateral force lack a corresponding Mg burst. Periods of rising lateral force correlate strongly with points where the diamond tip encounters visible cleavage steps. Significant fracture is observed at these points. When the stylus passes over the cleavage step, the lateral force falls sharply. Occasionally, the rapid tip displacement as the stylus passes over a cleavage step is followed by hopping motion for a millimeter or so, as in the latter portion of Fig. 2.

On polished surfaces, significant fluctuations in lateral force are relatively rare. Nevertheless, when they are observed, they are often accompanied by neutral Mg emission. Figure 3 shows Mg, lateral force, and displacement signals detected during abrasion of polished MgO with a diamond stylus at a normal load of 35 N. At comparable loads, Mg signals from the polished sample are much weaker ($<1\%$) than signals from as-cleaved samples. Further, autocatalytic-like behavior was not observed in Mg emissions from polished samples. In the case in Fig. 3, the emission rises sharply to a peak and decays gradually over the next several hundred microseconds. Nevertheless, the onset of Mg emission from both as-cleaved and polished samples coincides with drops in lateral force, i.e., slip-like events. On polished samples, these events can be observed even at low stylus velocities—here about 0.5 mm/s. Both polished and as-cleaved samples show weak, continuously decaying emissions at the end of the experiment. As noted below, these weak emissions are consistent with the emission of weakly bound species from the sample surface near room temperature.

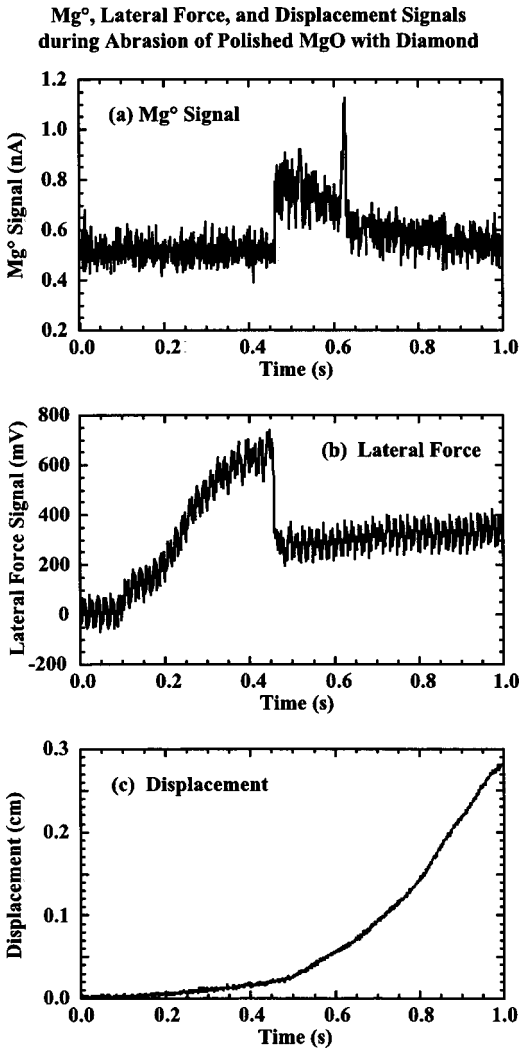

FIG. 3. (a) Neutral Mg, (b) lateral force, and (c) displacement signals during a single pass of a diamond tip across a cleaved MgO surface.

B. Mg emission during heating

Neutral Mg emissions are also observed when deformed MgO is heated in vacuum. Figure 4(a) shows a Mg signal acquired during heating of an indented, single crystal MgO sample as a function of the heater temperature, where the signal measured during an identical heating experiment without MgO was subtracted. Due to the significant thermal mass and conductivity of the sample, the temperature measured is somewhat higher than the actual sample temperature at the indent. Significant Mg emission is observed when the sample reaches about 1600 °C. Three Mg bursts are observed, each of which gradually builds to a peak, then drops suddenly. Thus the form of these bursts is remarkably similar to the autocatalytic-like bursts observed during abrasion.

Similar measurements performed with small, highly deformed MgO fragments in the heater are shown in Fig. 4(b). These submillimeter fragments were produced by scraping single crystal MgO in vacuum with a rough, steel file. This treatment produces extremely deformed MgO fragments, with all the deformed material located near the surface. The small size and heat capacity of these fragments minimize the difference between the sample and heater temperatures. Under these conditions, significant Mg emission was observed as the heater reached 500 °C. At 1300 °C, the emission intensity rises sharply offscale. This second rise in intensity presumably corresponds to the peak at 1600 °C from the indented sample. The bursts from the MgO fragments tend to be much smaller and lack the distinctive structure of autocatalytic-like bursts from indented MgO. We attribute the difference in the shape of these bursts to the small size of these fragments and to their corresponding dislocation structures.

Samples heated once to 1900–2000 °C showed little, if any, Mg when subsequently reheated. Signals detected from

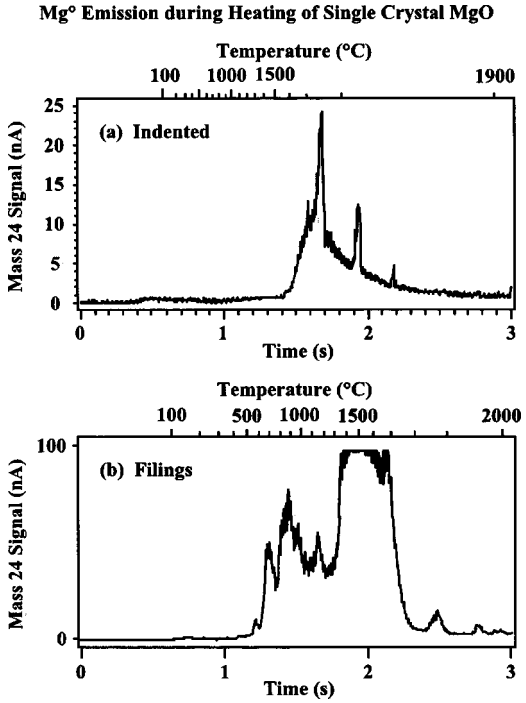

FIG. 4. Neutral Mg emission during heating of (a) an indented MgO crystal and (b) MgO fragments removed from a single crystal with a file-like device. The background signal observed during an identical heating program without MgO was subtracted from each signal. The temperature indicated by a Chromel–Alumel thermocouple attached to the resistance heater is indicated across the top of the diagram.

these annealed samples are virtually identical to signals detected with no MgO in the heater. Annealing removes most of the deformation-induced damage and eliminates subsequent Mg emission at the level of sensitivity attained in this work.

IV. DISCUSSION

A. Role of deformation

The wear of single crystal MgO has been well studied[16–19] due to its importance as a model semiplastic material. At modest loads, the passage of the stylus over a fresh portion of the substrate nucleates slip bands and causes existing slip bands to grow. On initially smooth surfaces, fracture is attributed to the interaction of mobile dislocations that form immobile dislocation structures. These serve as defects (stress concentrators) that raise the effective yield stress and ultimately nucleate crack growth.[20] Similar processes are responsible for the ultimate failure of many hard ceramics in wear applications. When the stylus encounters a cleavage step, the step itself is subjected to large forces and can be extensively deformed. Optical examination of the wear tracks produced in this work show extensive deformation and fracture, consistent with previous observations of wear along ⟨100⟩ directions.[17,18] In the present context, the fracture of deformed material provides an ideal environment for the emission mechanism proposed below, where dislocations introduced during wear are subsequently attracted to and emerge at these newly formed surfaces.

Bursts of neutral emissions have previously been observed following the fracture of single crystal alkali halides (NaCl and LiF),[8] and single crystal Ge.[9] These emissions are attributed to the energetic emergence of dislocations generated during fracture.[21,22] Initially driven into the bulk by the huge stress at the moving crack tip,[23,24] they subsequently return to the surface under the influence of image forces.[25] Simulations of the time required for dislocations generated during fracture to emerge from depths of a few microns are consistent with the observed millisecond intervals between fracture and the neutral emission bursts.[8] These emission bursts do not show autocatalytic-like behavior. Mg from MgO appears to be unique in this regard.

The role of dislocation structures in the emission process is further supported by the emission of Mg from heated, indented MgO in Fig. 4. Emission begins when the heater reaches a temperature of roughly 1600 °C, and subsequently shows emission spikes with characteristic autocatalytic-like time behavior. Comparison with emissions from abraded fragments suggests that the corresponding sample temperature is closer to 1300 °C. Although emission from abraded fragments begins at a much lower temperature, no autocatalytic-like bursts are observed at these lower temperatures. Thus the autocatalytic-like bursts appear to require somewhat extensive deformation, such as that produced by indentation or by the stylus encountering a cleavage step.

Cathodoluminescence images of indented MgO show changes in the appearance of slip bands around indents that begin at about 1200 °C.[26] Similarly, dislocation densities determined by microscopic observations of chemically etched surfaces begin to show decreased densities in deformed material after annealing to 1200 °C.[27] Thus the onset of significant Mg emission near 1300 °C in this work is consistent with the increased dislocation mobility expected at these temperatures. Significantly, most point defects, including isolated interstitial and vacancy centers, become mobile at much lower temperatures.[28,29]

X-ray topography measurements by Armstrong and Coworkers show strong evidence of the local relaxation of plastic strains around indents in MgO where dislocation interactions have induced cracking.[30–32] Sudden relaxation of dislocation pileups is expected to locally heat the surface—a special concern in the case of explosives and other especially reactive materials.[31,32] Sufficient heating could evaporate or sublimate weakly bound surface species. Such heating would also increase the dislocation mobility and promote further relaxation, possibly in an autocatalytic fashion, until relaxation is essentially complete.

In some configurations, emerging dislocations are especially well situated for the emission of neutral species. Dislocation motion in materials with a rock salt structure is largely confined to the {110} planes, with atomic motion along the ⟨110⟩ directions. Most fracture-related slip is confined to the {110} planes inclined 45° to the (100) cleavage surface, producing surface steps aligned along ⟨100⟩ directions. A schematic diagram of the surface structure produced by such a dislocation emerging to form an undercut step is shown in Fig. 5. The row of atoms along the advancing edge of the slip plane becomes mechanically as well as electro-

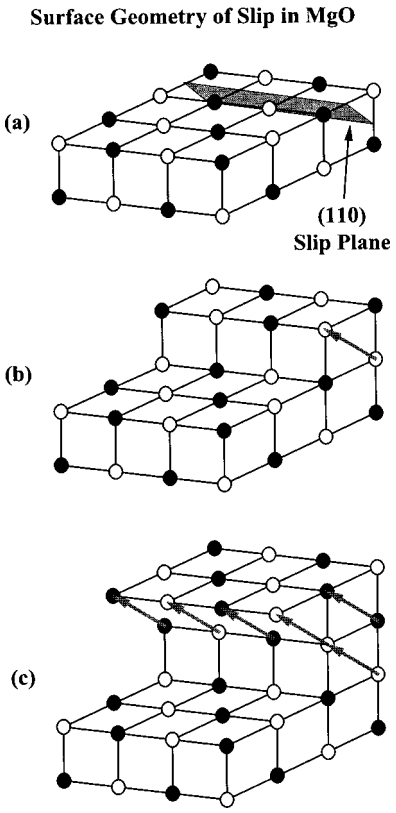

FIG. 5. Surface geometry of slip in crystals with the NaCl structure. (a) The top two layers of an undeformed crystal with a (110) slip plane marked in gray. (b) The crystal surface after slip has advanced one nearest neighbor unit (one Burgers vector). (c) The crystal surface after slip has advanced two units. The ions along the leading edge of the material that has slipped are extremely unstable.

statically unstable after slip has produced a step two nearest neighbor units high. Although many of the ions along the advancing edge would be redeposited onto the surface, neutralization (e.g., electron capture by Mg^+) would produce neutral atomic emissions.[33] By populating the surface with weakly bound species, emerging dislocations could also promote thermally stimulated emission processes.

Emission spikes from polished material are much smaller and lack the distinctive autocatalytic-like behavior of bursts from indented material. We attribute this to the sudden relaxation of dislocation structures which are too small or shallow to sustain the prolonged, gradually increasing emission required for autocatalytic-like bursts. In addition, more or less continuous emission persists for some hundreds of milliseconds after a slip-like event on the polished material. The gradual decay of continuous emission is consistent with exponential decay of weakly bound species due to thermally activated emission. (Assuming classical thermally activated emission with an attempt frequency of $10^{12}-10^{14}\,s^{-1}$, a time constant of a few hundred ms corresponds to activation energies of 0.6–0.8 eV, which seem quite reasonable.) Nevertheless, we cannot rule out continuous dislocation relaxation processes as a source of continuous emissions.

B. Role of point defects

Heated, abraded fragments yield Mg at about 500 °C, suggesting that the diffusion of point defects can also induce Mg emission. The internal chemistry of MgO crystals changes markedly near this temperature. Cation vacancies become mobile between 400 and 500 °C.[28] Impurity hydrogen becomes mobile near 400 °C,[34] and many cation impurities at somewhat higher temperatures (600 °C).[27] Significantly, oxygen vacancies (*F* centers) do not become mobile until about 900 °C.[35,36] Although *F* centers have been implicated in electron- and photon-stimulated emission of alkali metal atoms from alkali halides,[37,38] other processes appear to be responsible for the *onset* of Mg emission during heating.

Although several lattice defects become mobile at these low temperatures, the mobility of electronic defects may play a more important role in the onset of Mg emission. In particular, holes are released from several hole traps in the 400–600 °C range. As the temperature rises above about 500 °C, the equilibrium surface charge changes from negative to positive.[34] Electron spin resonance measurements show evidence of the oxidation of impurities in this temperature range.[35,39] At the surface, these mobile holes can react with surface oxygen ions and produce neutral O and oxygen vacancies.[34] This process erodes the anion sublattice and eventually destabilizes surface Mg^{2+}. After capturing nearby electrons to form neutral Mg, neutral Mg can be emitted thermally. (In the alkali halides, similar processes in the bulk produce alkali metal colloids during electron irradiation.) In this work, the emission of atomic O (16 amu) was not studied because this signal is complicated by the production of atomic O by electron-impact ionization of CO and O_2. Strong CO and O_2 signals are observed when MgO particles are heated above 500 (CO) and 900 °C (O_2), presumably due to hole capture reactions similar to those proposed for O emission.[40]

In previous work, we found evidence that transient heating produces reduced Mg species on cleaved MgO surfaces, consistent with this scenario.[41] Surfaces exposed to a single, 30 ns pulse of 248 nm laser radiation at a laser power density just below the damage threshold display patches of magnesium-rich droplets. Significantly, these droplets are confined to elliptical melted patches along the surface. This distribution is strongly suggestive of localized heating where dislocations intersect the surface. Cleavage-induced dislocations in MgO are efficient recombination centers that are preferentially heated by the decay of laser-induced excitations (exciton decay or electron–hole recombination). It is not clear whether the decay of thermally induced electronic defects might produce localized hot spots as MgO is heated in the 500–600 °C range. Any reduced Mg on the surface at this temperature would be vulnerable to thermal emission processes. At 500 °C, the vapor pressure of metallic Mg is approximately 1 Pa. Even one 10 μm^2 patch of metallic Mg would produce a detectable Mg signal.

Weakly bound species, such as reduced Mg, are of considerable interest in terms of surface chemistry. Defects on MgO surfaces in particular have been the subject of intensive theoretical investigation.[42–49] Weakly adsorbed species[50] play an important role in laser-induced emissions from MgO and other ionic materials.[14,51–56] Measurements of laser-induced neutral emissions from NaCl, LiF, and MgO suggest

that weakly bound neutral species continue to be emitted long after the laser pulse—often for many milliseconds. At high laser power densities, material evaporated by the laser pulse can be redeposited onto the surface.[57] Thermal processes can remove the more weakly bound species over the course of milliseconds after the laser pulse, even at room temperature.[33] Similar species undoubtedly contribute to the emissions observed in this work, even if the emission kinetics are controlled by the relaxation of deformation-related structures. Weakly adsorbed species would also strongly enhance the chemical reactivity of tribologically stimulated surfaces and possibly contribute to tribochemical reactions.[58]

C. Effect of other material properties

Among the materials studied to date, the autocatalytic-like behavior of Mg emission from MgO after fracture, during abrasion, and during the heating of indented material is unique. Alkali emissions from the alkali halides, for instance, do not show this behavior.[8] Nor do other emissions from MgO. To allow for autocatalytic-like behavior, the participating dislocation structures must be able to relax gradually. These structures must be stable enough to resist immediate relaxation, but not so stable as to prevent relaxation altogether. Although other examples of autocatatlyic behavior may ultimately be found, the unique behavior of MgO requires some explanation.

Among ionic materials with the rock salt structure, MgO is remarkably stiff, with a directionally averaged Young's modulus of about 300 GPa and shear modulus of 140 GPa.[59] Thus the strain energy associated with deformation is likely to be unusually high. Further, deformation is more constrained in MgO than in the alkali halides, the most similar materials under study. While deformation in both MgO and NaCl is largely confined to the $\langle 101\rangle\{10\underline{1}\}$ system, NaCl is capable of slip on the $\langle 101\rangle\{111\}$ system.[60] This additional degree of freedom minimizes deformation-related stress concentrations in NaCl and reduces the amount of cracking during indentation. Although the elastic strain surrounding indents on NaCl is negligible relative to plastic strain (at maximum indenter penetration), the elastic strain surrounding indents in MgO can easily reach 10%.[60] Significantly, the plastic strain surrounding indents in MgO relaxes significantly when the indentor is removed—recovery which requires large numbers of dislocations to return to the surface.[60] As noted above, recovery of plastic strain along indentation-related cracks is considered to be a potential source of local, transient heating.[31]

Thus the lack of autocatalytic-like emission bursts in NaCl and similar materials may be attributed to the much smaller elastic strain surrounding deformed material and the increased difficulty of forming deformation-related cracks. Isolated dislocation structures would still be drawn back to the surface by image forces, but they would not experience the strong additional elastic force present in MgO. Deformation-induced cracks pass through severely deformed material that would be ideal sources of emission. Such cracks are much more common in MgO than in alkali halides.

Similar considerations may account for the lack of autocatalytic-like emissions from single crystal germanium,[9] calcite, and sodium nitrate.[11] These are significantly softer and less stiff than MgO. As with the alkali halides, the elastic stress surrounding major deformation structures is likely to be small. The covalent bonding and diamond structure of germanium may also hinder cross slip, which is responsible for the extended deformation structures (slip bands) in MgO and alkali halides. Again, deformation structures are still attracted to the surface by image forces and can yield sharp emission bursts, but not prolonged, autocatalytic-like bursts.

V. CONCLUSIONS

Abrasion of MgO by diamond in vacuum produces bursts of neutral Mg emission with a distinctive time behavior. Discrete slip events are accompanied by weak emissions which gradually grow to a peak, then fall dramatically. We attribute these emissions to the energetic relaxation of dislocation structures to the surface. In contrast to relaxation in alkali halides, this relaxation starts slowly and gradually accelerates to completion. Similar bursts of neutral Mg are observed when indented single crystal MgO is heated to temperatures above 1300 °C. At these temperatures, dislocations in highly deformed material become much more mobile. The growth of cracks through highly deformed material would provide an ideal situation for this emission process.

Locally, the relaxation of dislocation-related structures during abrasion and wear alters the surface with violence comparable to initial deformation. Given the high reactivity of neutral Mg and the presence of corresponding vacancy defects on the surface, these processes may dramatically alter the surface chemistry. In principle, such reactive species may have deleterious effects on lubricants. Spikes in transient temperature, possibly extreme, are also expected near the relaxed material. These spikes in temperature would alter the kinetic energy distribution of any emitted particles, which can in principle be measured. Neutral emissions during abrasion depend strongly on chemical as well as mechanical processes at and near the surface. Understanding these emissions and the processes that produce them will facilitate their use as a unique probe of abrasion and wear.

ACKNOWLEDGMENTS

This work was supported by the National Science Foundation under Grant No. CMS-01-16196, an associated Research Experiences for Undergraduates supplement, by the Department of Energy Grant No. DE-FG03-02ER45988, by a subcontract with the University of Florida for NSF Knowledge and Distributed Intelligence collaboration under Grant No. 9980015, and by the Yonam Foundation.

[1] J. T. Dickinson, in *Non-Destructive Testing of Fibre-Reinforced Plastic Composites*, edited by J. Summerscales (Elsevier Applied Science, London, 1990), p. 429.
[2] J. T. Dickinson, S. C. Langford, and L. C. Jensen, in *Fracture Mechanics of Ceramics 10: Fracture Fundamentals, High-Temperature Deformation, Damage, and Design*, edited by R. C. Brandt, D. P. H. Hasselman, D. Munz *et al.* (Plenum, New York, 1992), Vol. 10, p. 1.
[3] J. T. Dickinson, S. C. Langford, S. Nakahara, L. Scudiero, M.-W. Kim, and N. S. Park, in *Fractography of Glasses and Ceramics III*, edited by J.

R. Varner, V. D. Fréchette, and G. D. Quinn (American Ceramic Society, Westerville, OH, 1996), Vol. 64, p. 193.
[4] J. T. Dickinson, in *Encyclopedia of Materials: Science and Technology*, edited by K. H. Jürgen Buschow, R. W. Cahn, M. C. Flemings, B. Ilschner, E. J. Kramer, and S. Mahajan (Elsevier, London, 2001).
[5] G. P. Williams and T. J. Turner, Solid State Commun. **29**, 201 (1979).
[6] S. C. Langford, J. T. Dickinson, and L. C. Jensen, J. Appl. Phys. **62**, 1437 (1987).
[7] M.-W. Kim, S. C. Langford, and J. T. Dickinson, Tribol. Lett. **1**, 147 (1995).
[8] J. T. Dickinson, L. C. Jensen, S. C. Langford, and J. P. Hirth, J. Mater. Res. **6**, 112 (1991).
[9] J. T. Dickinson, S. C. Langford, and L. C. Jensen, Phys. Rev. Lett. **66**, 2120 (1991).
[10] S. C. Langford, L. C. Jensen, J. T. Dickinson, and L. R. Pederson, J. Mater. Res. **6**, 1358 (1991).
[11] J. T. Dickinson, L. C. Jensen, S. C. Langford, P. E. Rosenberg, and D. L. Blanchard, Phys. Chem. Miner. **18**, 320 (1991).
[12] J. T. Dickinson, L. C. Jensen, M. R. McKay, and F. Freund, J. Vac. Sci. Technol. A **4**, 1648 (1986).
[13] J. T. Dickinson, L. C. Jensen, and M. R. McKay, J. Vac. Sci. Technol. A **5**, 1162 (1987).
[14] J. J. Shin, M.-W. Kim, and J. T. Dickinson, J. Appl. Phys. **80**, 7065 (1996).
[15] J. T. Dickinson, L. C. Jensen, S. C. Langford, P. E. Rosenberg, and D. L. Blanchard, Phys. Chem. Miner. **18**, 453 (1992).
[16] R. P. Steijn, Wear **7**, 48 (1964).
[17] C. A. Brookes and J. B. O'Neill, in *Anisotropy in Single-Crystal Refractory Compounds*, edited by F. W. Vahdiek and S. A. Mersol (Plenum, New York, 1968), p. 291.
[18] T. Sugita and T. Hasegawa, J. Mater. Sci. **13**, 1471 (1978).
[19] N. W. J. Brooks, R. A. Duckett, and I. M. Ward, J. Polym. Sci., Part B: Polym. Phys. **36**, 2177 (1998).
[20] C. A. Brookes, M. P. Shaw, and P. E. Turner, Proc. R. Soc. London, Ser. A **409**, 141 (1987).
[21] J. J. Gilman, Trans. Metall. Soc. AIME **212**, 310 (1958).
[22] S. J. Burns, Scr. Metall. **20**, 1489 (1986).
[23] S. J. Burns and W. W. Webb, J. Appl. Phys. **41**, 2086 (1970).
[24] S. J. Burns and W. W. Webb, J. Appl. Phys. **41**, 2078 (1970).
[25] J. P. Hirth and J. Lothe, *Theory of Dislocations*, 2nd ed. (Wiley, New York, 1982).
[26] J. Llopis, C. Ballesteros, J. Piqueras, A. Remon, and R. González, Phys. Status Solidi A **78**, 679 (1983).
[27] R. J. Stokes and C. H. Li, Discuss. Faraday Soc. **38**, 233 (1964).
[28] J. E. Wertz, J. W. Orton, and P. Auzins, Discuss. Faraday Soc. **31**, 140 (1961).
[29] Y. Chen, R. T. Williams, and W. A. Sibley, Phys. Rev. **182**, 960 (1969).
[30] R. W. Armstrong, C. S. Coffey, and W. L. Elban, Acta Metall. **30**, 2111 (1982).
[31] R. W. Armstrong and W. L. Elban, in *Microindentation Techniques in Materials Science and Engineering*, edited by P. J. Blau and B. R. Lawn (American Society for Testing and Evaluation, Philadelphia, PA, 1986), Vol. 889, p. 109.
[32] R. W. Armstrong and W. L. Elban, Mater. Sci. Eng., A **111**, 35 (1989).
[33] J. J. Shin, J. T. Dickinson, L. C. Jensen, and S. C. Langford (unpublished).
[34] M. M. Freund, F. Freund, and F. Batllo, Phys. Rev. Lett. **63**, 2096 (1989).
[35] W. A. Sibley, J. L. Kolopus, and W. C. Mallard, Phys. Status Solidi **31**, 223 (1969).
[36] Y. Chen, J. L. Kolopus, and W. A. Sibley, Phys. Rev. **186**, 865 (1969).
[37] G. M. Loubriel, Phys. Rev. Lett. **57**, 1781 (1986).
[38] G. M. Lourbriel, T. A. Green, N. H. Tok, and J. R. F. Haglund, J. Vac. Sci. Technol. B **5**, 1514 (1987).
[39] B. V. King and F. Freund, Phys. Rev. **29**, 5814 (1984).
[40] R. Knobel and F. Freund, MRS Bull. **15**, 1247 (1980).
[41] J. T. Dickinson, L. C. Jensen, R. L. Webb, M. L. Dawes, and S. C. Langford, J. Appl. Phys. **74**, 3758 (1993).
[42] John M. Vail, J. Phys. Chem. Solids **51**, 589 (1990).
[43] A. Gibson, R. Haydock, and J. P. LaFemina, Appl. Surf. Sci. **72**, 285 (1993).
[44] R. Nada, A. C. Hess, and C. Pisani, Surf. Sci. **336**, 353 (1995).
[45] L. N. Kantorovich, J. M. Holender, and M. J. Gillan, Surf. Sci. **343**, 221 (1995).
[46] A. M. Ferrari and G. Pacchioni, J. Phys. Chem. **100**, 9032 (1996).
[47] E. A. Kotomin, M. M. Kuklja, R. I. Eglitis, and A. I. Popov, Mater. Sci. Eng., B **37**, 212 (1996).
[48] P. V. Sushko and A. L. Shulger, Surf. Sci. **421**, L157 (1999).
[49] A. L. Shluger, P. V. Sushko, and L. N. Kantorovich, Phys. Rev. B **59**, 2417 (1999).
[50] D. Murphy and E. Giamello, J. Phys. Chem. **99**, 15172 (1995).
[51] R. L. Webb, L. C. Jensen, S. C. Langford, and J. T. Dickcinson, J. Appl. Phys. **74**, 2323 (1993).
[52] R. L. Webb, L. C. Jensen, S. C. Langford, and J. T. Dickson, J. Appl. Phys. **74**, 2338 (1993).
[53] D. R. Ermer, J.-J. Shin, S. C. Langford, K. W. Hipps, and J. T. Dickinson, J. Appl. Phys. **80**, 6452 (1996).
[54] J. J. Shin, D. R. Ermer, S. C. Langford, and J. T. Dickinson, Appl. Phys. A: Mater. Sci. Process. **64**, 7 (1997).
[55] C. Bandis, S. C. Langford, J. T. Dickinson, D. R. Ermer, and N. Itoh, J. Appl. Phys. **87**, 1522 (2000).
[56] S. Kano, S. C. Langford, and J. T. Dickinson, J. Appl. Phys. **89**, 2950 (2001).
[57] R. Kelly, J. Chem. Phys. **92**, 5047 (1990).
[58] V. J. Novotny, X. Pan, and C. S. Bhatia, J. Vac. Sci. Technol. A **12**, 2879 (1994).
[59] D. H. Chung and W. R. Buessem, in *Anisotropy in Single-Crystal Refractory Compounds*, edited by F. W. Vahldiek and S. A. Mersol (Plenum, New York, 1968), p. 217.
[60] R. W. Armstrong and C. Cm. Wu, J. Am. Ceram. Soc. **61**, 102 (1978).