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The Structure and Reactivity of Boron Surfaces - Final Technical Report

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This is the final technical report on a project designed to apply the experimental techniques of modern surface science to address issues loosely related to the combustion of boron particles. Boron particles have potential application as a fuel. Our experiments focused on the reaction of O_2 with the (111) surface of β-rhombohedral boron to produce B_2O_3 and the subsequent reactions involved in desorbing B_2O_3 from the boron surface. We find that the reactivity with O_2 is low throughout the temperature range of 300-1300 K. We find that the net uptake of O by the surface is at a maximum in the temperature range of 800-1100 K but that at most only submonolayers of B_2O_3 are formed. When B_2O_3 is directly deposited on the surface, it reacts with the substrate in the temperature range of 1100 to 1300 K to produce B_2O_2. In separate experiments, we have used scanning tunneling microscopy to obtain atomically resolved images of the $LaB_6(100)$ surface.

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COMPLETED PROJECT SUMMARY

Title: The Structure and Reactivity of Boron Surfaces

Principle Investigator: Professor Michael Trenary
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University of Illinois at Chicago
Chicago, IL 60680

Inclusive Dates: 1 January 1988 - 31 August 1991

Grant Number: AFOSR 88-0111

Yearly Costs:		
	01/01/88 - 12/31/88	$144,250.00
	01/01/89 - 12/31/89	$141,320.00
	01/01/90 - 8/31/91	$81,600.00
	Total Cost	$367,170.00

Junior Research Personnel:

Shoudeng Liang   Wei Cho Foo
John S. Ozcomert   Yajun Wang

Research Objective:

    To apply the methods of modern surface science to the problem of the surface oxidation of elemental boron. Implicit in this goal was the need to construct a dedicated apparatus for boron surface science studies and to establish the experimental procedures needed to perform surface science studies on small single crystals of elemental boron. The experiments were designed to gain a detailed understanding of the reaction of O_2 with a boron surface to form boron oxides including B_2O_3 and to gain an understanding of the desorption of a B_2O_3 layer on top of the boron substrate. In the final phase scanning tunneling microscopy was to be applied to the surface properties of boron and related materials.

Publications:

"The Reactions of B_2O_3 and O_2 with the β-Rhombohedral Boron (111) Surface", Wei Cho Foo, John S. Ozcomert and Michael Trenary, in Boron-Rich Solids, (AIP Conference Proceedings 231), D. Emin, T. L. Aselage, A. C. Switendick, B. Morosin, C. L. Beckel, eds., (American Institute of Physics, New York 1991) p. 643

"The Oxidation of the β-Rhombohedral Boron (111) Surface", Wei Cho Foo, John S. Ozcomert, and Michael Trenary, Surf. Sci. **255**, 245 (1991)

92-05617

Summary of accomplishments:

1) An apparatus was constructed for the long-term study of the surface properties of boron and the boron-rich solids.

2) Experimental procedures for performing surface science experiments on a single crystal (111) surface of β-rhombohedral boron were developed. In particular, the procedure required to obtain a clean, well-ordered surface of boron under ultrahigh vacuum conditions was established.

3) The reaction between O_2 and the (111) surface of β-rhombohedral boron was studied between room temperature and 1200 K. A low reactivity was found at room temperature which increased only modestly at elevated temperatures. Even at temperatures between 900-1100 K where the reactivity was highest, only submonolayers of B_2O_3 are formed on the boron surface.

4) The reaction between the boron substrate and multilayers of isotopically pure $^{10}B_2O_3$ directly deposited on the boron surface was studied. It was found that the deposited B_2O_3 reacts with the substrate to produce B_2O_2 leading to the net removal of substrate boron. The B_2O_2 produced displayed a natural abundance ratio of $^{11}B/^{10}B$ indicating extensive reaction with the substrate. These experiments demonstrate that surface B_2O_3 produced in the oxidation of boron does not act as a passive coating but will be reduced by the boron substrate.

5) Procedures were established for conducting scanning tunneling microcopy experiments under UHV conditions in the apparatus constructed for the boron studies. The ability to obtain atomically resolved STM images of a boron-rich solid under UHV conditions was demonstrated for the LaB_6(100) surface. The structural and bonding properties of pure boron and the boron-rich solids are similar. The issues that this project was initially designed to address on boron surfaces apply equally well to any of the boron-rich solids including the rare earth hexaborides.

The Structure and Reactivity of Boron Surfaces

Final Technical Report for AFOSR Grant 88-0111

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Abstract

This is the final technical report on a project designed to apply the experimental techniques of modern surface science to address issues loosely related to the combustion of boron particles. Boron particles have potential application as a fuel. Our experiments focused on the reaction of O_2 with the (111) surface of β-rhombohedral boron to produce B_2O_3 and the subsequent reactions involved in desorbing B_2O_3 from the boron surface. We find that the reactivity with O_2 is low throughout the temperature range of 300-1300 K. We find that the net uptake of O by the surface is at a maximum in the temperature range of 800-1100 K but that at most only submonolayers of B_2O_3 are formed. When B_2O_3 is directly deposited on the surface, it reacts with the substrate in the temperature range of 1100 to 1300 K to produce B_2O_2. In separate experiments, we have used scanning tunneling microscopy to obtain atomically resolved images of the LaB_6(100) surface.

Introduction

Boron and the boron-rich solids, which include many of the metal borides, constitute a class of materials with unique structural properties. Common to all of the metal borides are electron deficient lattices of covalently bonded boron atoms that are stabilized by electron donation from the metal. These materials are generally extremely hard yet brittle, and have high melting points; these properties are largely a consequence of the nature of the rigid boron networks. Even when the bulk crystal structures are as complex as in YB_{66} with roughly 1600 atoms per unit cell, macroscopic single crystals can often be prepared[1] and precise crystal structures determined. However, in contrast to the rather well-characterized bulk structures, relatively little is known about the surface crystallography.

The structural chemistry of pure boron itself is characterized by three-center two-electron bonds and the wide use of icosahedral B_{12} units. Studies of the novel bonding exhibited in boron compounds have expanded our understanding of chemical bonding in general[2]. The intriguing aspects of boron structural chemistry have motivated detailed studies of boron compounds and of boron-rich solids, including the various forms of elemental boron[1,3]. One area of boron chemistry which has received almost no attention is the surface properties of the solid element. Given the unique structures displayed by boron containing materials, one would expect unique structural and bonding properties of boron surfaces.

A more applied interest in the oxidation of boron surfaces stems from the high heat of formation of $\approx$ -300 Kcal/mole for B_2O_3. This makes boron attractive as a fuel[4] and has led to several studies of the combustion of boron[5-11]. In an early and influential study, Macek and Semple[6] used high speed photography to follow the burning of boron particles injected into streams of oxidizing gases in the temperature range of 1800 to 2900 K. They observed that a boron particle burns in two stages. It first ignites, burns brightly but briefly and then extinguishes. In the second stage the particle reignites and burns more brightly and to completion. Based on these observations, Macek and Semple and others[6-11] have concluded that the surface of the boron particle is coated with B_2O_3 and that the second stage of burning does not take place until this oxide layer evaporates. Furthermore, it is assumed that the boron particles are initially coated with a thick oxide layer. These assumptions are reasonable given the high melting point of boron of $\approx$ 2360 K and the low melting point of B_2O_3 of 720 K. However, it should be stressed that the assumption of a B_2O_3 surface coating on a burning boron particle is not based on any direct surface probes but rather on indirect inference. Thus, fundamental surface science studies of the reaction of O_2 and B_2O_3 with the surface of elemental boron are highly relevant to boron combustion. Another important observation is that crystalline boron particles are much less reactive than amorphous boron particles[8]. This

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suggests that boron surface structure plays an important role in boron oxidation. It is therefore highly desirable to perform experiments on well-characterized single crystal surfaces.

A metal boride which has an important technological application is lanthanum hexaboride. This material is similar to the other lanthanide metal hexaborides in that it has a high melting point, a low work function and metallic conduction. These properties have led to the wide-spread use of LaB_6 cathodes as thermionic emitters. Like other boron-rich solids, the properties of LaB_6 stem largely from the nature of the covalently bonded boron atoms. Thus we expect that the surface properties of LaB_6 will also be largely determined by the structural properties of boron.

In the period covered in this grant we have 1) constructed a permanent apparatus with an expected useful lifetime of 15-20 years dedicated to surface studies of elemental boron and of the boron rich solids, 2) used X-ray photoelectron spectroscopy and low energy electron diffraction to establish procedures for obtaining a clean well-ordered (111) surface of β-rhombohedral boron, 3) used temperature programmed desorption and XPS to study the reaction of the (111) surface of β-rhombohedral boron with O_2 and B_2O_3, and 3) successfully used scanning tunneling microscopy (STM) to obtain atomic scale structural information on the LaB_6(100) surface.

The Experimental Apparatus

The main apparatus used in these experiments is described in detail in ref 12. It consists of a cylindrical stainless steel vacuum chamber equipped with a quadrupole mass spectrometer, low energy electron diffraction optics, a hemispherical electron energy analyzer and a dual Mg/Al anode X-ray source. The entire chamber rests on an air table (Barry Control) to isolate the chamber from building vibrations as required for STM experiments. Our STM was manufactured by McAllister Technical Services and is based on a piezoelectric tube scanner. Sample positioning is achieved inertially with a second larger diameter piezoelectric tube. This STM allows for easy transfer of the sample to our main manipulator which in turn will allow access to all instruments on the chamber.

For multiplexed temperature programmed desorption, we have interfaced our UTI 100C quadrupole mass spectrometer to an IBM AT compatible computer. The interface electronics were constructed here and the software was developed by the graduate students on this project. We also constructed a programmable temperature controller using a PID algorithm to linearize the temperature ramp. The controller drives a 50 amp power supply for resistive heating of the sample. We also have a power supply which allows us to float a filament at 5 kV for electron bombardment heating of our sample. The mass spectrometer interface, the programmable temperature controller and the electron bombardment supply were all constructed in our departmental electronics shop.

Boron Crystal Preparation

The details of crystal preparation and cleaning have been published[12]. We purchased two 8-9 cm long boron rods, 5.5 and 6 mm in diameter originally grown by Wacker Chemitronic of Munich, Germany. To the best of our knowledge no commercial source currently exists. The crystals were oriented to within 0.5° of the rhombohedral [111] direction using Laue back reflection X-ray diffraction. Disk shaped slices of the boules were obtained using a thin diamond circular blade saw. Because of the brittleness of crystalline boron, cracking of the disks frequently occurred. Thus we worked with both disks of the full diameter of the boules as well as partial disks. In either case, the crystals were polished using increasingly finer diamond polishing compound down to a diamond particle size of 1.0 micron. Because of the hardness of boron, it was relatively easy to obtain a scratch free reflective surface. However, the crystal face did show deep circular pits of approximately 0.25 micron diameter as revealed by electron microscopy.

For mounting in the UHV chamber the crystals were attached to a tantalum disk of approximately the same size as the boron. A 0.1 mm 5%Re-W/26%Re-W thermocouple was attached to the top of the crystal. The temperatures obtained with the thermocouple were calibrated with an optical pyrometer. Cleaning of the crystal in the vacuum chamber was achieved by heating to 1400-1800 K and was monitored with XPS. The principle contaminants are carbon, indicated by the C(1s) peak at 284 eV and oxygen with the O(1s) peak at 532 eV. Based on the sensitivity factors for oxygen and carbon relative to boron we can routinely obtain oxygen and carbon impurity levels less than 1% of the amount of boron.

The Reaction with O_2

The details of our study of the reaction of O_2 with the (111) surface of β-rhombohedral boron have been published in full in ref 12 and a preliminary report appears in ref. 13. Therefore, only a brief summary of the study is given here. We found that the reaction with O_2 proceeds in two stages, an initial uptake in oxygen followed by a much slower increase in surface oxygen. The net oxygen uptake is low at room temperature, reaches a maximum at 1000-1100 K, and then falls to a low level at 1273 K. To calibrate the oxygen coverage, XPS spectra of the O_2 exposed surface were compared with spectra of B_2O_3 multilayers directly deposited on the surface. The comparison indicates that only submonolayer oxygen coverages are achieved under the conditions used.

The Reaction with B_2O_3

The details of our study of the reaction of isotopically pure $^{10}B_2O_3$ with the (111) surface of β-rhombohedral boron using

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temperature programmed desorption is contained in a paper (ref 14) that has been accepted for publication in Surface Science and is scheduled to appear in January or February of 1992. A brief preliminary account of the results appears in ref. 13. Therefore only a brief description is given here. The $^{10}B_2O_3$ was directly deposited on the boron surface from a Knudsen cell operated at 1200 K. The boron crystal contained the natural abundance ratio of the $^{11}B:^{10}B$ isotopes of 4:1. The thermal desorption results show a B_2O_3 peak near 1200 K consisting solely of the $^{10}B_2O_3$ isotope followed by B_2O_2 and B_2O_3 peaks in the range 1300-1350 K with a $B_2O_2:B_2O_3$ peak area ratio of about 2:1. The higher temperature B_2O_2 and B_2O_3 desorption peaks follow zero-order desorption kinetics with an activation energy of 554±41 kJ mol^{-1}. The higher temperature peaks show substantial incorporation of the ^{11}B isotope from the substrate. The results are consistent with a reaction mechanism in which boron from the substrate first dissolves in the molten B_2O_3 layer and then reacts to form a B_6O suboxide which then decomposes to yield B_2O_3 and B_2O_2. However, we have no direct evidence for the presence of the B_6O suboxide on the surface.

<u>STM Studies of LaB$_6$(100)</u>

In order to establish that our STM was indeed capable of atomic resolution in UHV as well as to calibrate our piezoelectric expansion coefficients it was important to obtain images of a surface, Si(111)-7x7, which had been extensively studied in the past by other groups. The images that we have obtained of this Si surface are of comparable quality to those published by other groups. We used our Si images to calibrate the x, y piezo-electric expansion coefficients based on a unit cell length of 26.9 Å[20] for Si(111)-7x7. The observation of monatomic steps on the Si surface allowed for calibration of our z expansion coefficient. In addition, observation of the Si(111)-7x7 LEED pattern enabled the diameter of our LEED screen to be calibrated so that accurate surface lattice constants could be obtained from the observed LaB$_6$(100) LEED patterns.

We have studied the LaB$_6$(100) surface using scanning tunneling microscopy (STM) and low energy electron diffraction (LEED). A cut and polished LaB$_6$(100) disk, 1 mm thick and 3 mm in diameter, was purchased from FEI, Inc., of Beaverton, OR. We observe a surface with a square lattice of La atoms having a 4 Å spacing with approximately 10% of the La surface sites vacant. As indicated by a weak atomic corrugation of only 0.2 Å, the electronic states at the surface near the Fermi level display a degree of delocalization typical of a metal. On a larger scale, the surface is observed to consist of (100) terraces with an average width of 125 Å separated by steps one unit cell high.

The student who obtained the LaB$_6$(100) results, John Ozcomert, presented a paper on his work on November 14 at the national meeting of the American Vacuum Society in Seattle. That paper, ref. 15, has been accepted for publication in the Journal

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of the American Vacuum Society. We intend to submit a short description of the work to Applied Physics Letters in the near future.

Conclusions

Through our studies of the (111) surface of β-rhombohedral boron we have successfully used the techniques of surface science to explore the reaction of O_2 with solid boron to produce B_2O_3. Our results demonstrate that despite the high exothermicity of the reaction

$$4B(s) + 3O_2 \rightarrow 2B_2O_3$$

a clean well-ordered (111) surface of β-rhombohedral boron displays a relatively low reactivity towards O_2. By comparing the results of a surface oxidized with O_2 to a surface on which B_2O_3 had been directly deposited, we conclude that the reaction with O_2 produces at most only a submonolayer coverage of B_2O_3. This is in marked contrast to studies of burning boron particles in which the observed behavior was assumed to be due to the formation of a thick coating of molten B_2O_3 on the boron particle surface. Our thermal desorption studies of directly deposited B_2O_3 indicate that rather than acting simply as a passive barrier to further boron oxidation, B_2O_3 itself can react with the boron substrate to produce B_2O_2. This in turn suggests that B_2O_2 may be a substantial product of the reaction of boron with O_2. Since the heat of formation of B_2O_2 is substantially lower than that of B_2O_3, the energy released by burning boron would be less than expected based on formation of B_2O_3 only. This finding has obvious important implications for the use of boron as a fuel. We would hope that our experimental results will influence future modelling efforts to include the reaction of B_2O_3 with boron to produce B_2O_2.

This project represents the first step of my long-range goal of developing a new field of research; the surface science of boron and the boron-rich solids. The elemental forms of boron and the boron-rich solids possess common structural, physical and chemical properties. A key goal of this research is to establish the relationship between the surface structural properties possessed by these materials and the chemical reactivity of these structures. The use of scanning tunneling microscopy, will be central to this goal. Our successful use of STM to examine the LaB_6(100) surface is therefore a significant milestone in the development of this field.

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References

1. J. L. Hoard and R. E. Hughes, in **The Chemistry of Boron and Its Compounds**, E. L. Muetterties, ed., (Wiley, New York, 1967); D. Emin, et. al., eds., **Boron-Rich Solids,** AIP Conf. Proc. 231, (Am. Inst. Phys., New York, 1991).
2. W. N. Lipscomb, Science $\underline{196}$ (1977) 1047; J. Less-Common Metals, $\underline{81}$ (1981) 1
3. H. Werheit, Ed., Proc. 9th Int. Symp. on Boron, Borides and Rel. Compounds, Univ. Duisburg, Germany, 1987
4. M. L. King, J. Spacecraft, $\underline{19}$ (1982) 294
5. C. P. Talley, Aero/Space Eng. $\underline{18}$ (1959) 37
6. A. Macek and J. M. Semple, Comb. Sci. and Tech. $\underline{1}$ (1969) 181
7. A. Macek and J. M. Semple, Proc. 13th Symp. (Int.) on Combustion, The Combustion Institute, Pittsburgh, PA, 1970, pp. 859-8687.
8. G. Mohan and F. A. Williams, AIAA J. $\underline{10}$ (1972) 776
9. S. C. Li, F. A. Williams, and F. Takahshi, Proc. 22th Symp. (Int.) on Combustion, The Combustion Institute, Pittsburgh, PA, 1988, pp. 1951-1960
10. I. Glassman, F. A. Williams, and P. Antaki, Proc. 20th Symp. (Int.) on Combustion, The Combustion Institute, Pittsburgh, PA, 1984, pp. 2057-2064
11. R. A. Yetter, S. Y. Cho, H. Rabitz, F. L. Dryer, R. C. Brown, and C. E. Kolb, Proc. 22th Symp. (Int.) on Combustion, The Combustion Institute, Pittsburgh, PA, 1988, pp. 919-929
12. W. C. Foo, J. S. Ozcomert, and M. Trenary, Surf. Sci. $\underline{255}$, 245 (1991)
13. W. C. Foo, J. S. Ozcomert, and M. Trenary, in Boron-Rich Solids, (AIP Conference Proceedings 231), D. Emin, T. L. Aselage, A. C. Switendick, B. Morosin, C. L. Beckel, eds., (American Institute of Physics, New York 1991) p. 643
14. W. C. Foo, J. S. Ozcomert, and M. Trenary, Surf. Sci., In press (Accepted, September 20, 1991)
15. J. S. Ozcomert and M. Trenary, J. Vac. Sci. Technol., In press, (Accepted, November 18, 1991)