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MATERIALS RESEARCH FOR ADVANCED INERTIAL INSTRUMENTATION

TASK 2: GAS BEARING MATERIAL DEVELOPMENT BY SURFACE MODIFICATION OF BERYLLIUM

TECHNICAL REPORT NO. 1
FOR THE PERIOD
30 SEPTEMBER 1977 – 30 JUNE 1978

By

JOHN R. PALMIERI

Prepared for the Office of Naval Research, Department of the Navy, Under Contract N00014-77-C-0388.

The Charles Stark Draper Laboratory, Inc.
Cambridge, Massachusetts 02139

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Beryllium surfaces, such as used in inertial instrument gas bearings, are to be modified for improved friction and wear performance by case hardening with boron. Techniques being investigated are (1) high temperature reactive diffusion of the elements, and (2) low temperature ion implantation of boron into beryllium.

Diffusion experiments to date have consisted of heating the solid elements in contact with each other under inert atmosphere at temperatures predicted by the Be-B phase diagram to avoid undesirable eutectic reactions. Of the two elements, beryllium has been used as a bulk solid and boron has been applied to its surface from a powder slurry, sputtered film, or bulk solid. Preliminary experiments have been done with CVD of boron from a commercial boronizing compound during induction heating under argon. Results →

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SECURITY CLASSIFICATION OF THIS PAGE *(When Data Entered)* indicate that a vapor source of boron may react differently as compared to a solid boron source with a beryllium substrate in that adherent compounds are formed.

Ion implantation of boron into beryllium has been attempted. Initial beryllium flat specimens have had a concentration of 10 atomic percent boron implanted to a depth of approximately a micron. Annealing these specimens up to 650° C appears to have increased microhardness and resulted in a metallographic change resembling precipitation of a second phase. Analysis of this reaction is in progress. Higher concentrations of implanted boron (>30 atomic percent) are planned.

R-1199

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APPROVED: M S Sapuppo
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SECTION 1

INTRODUCTION

Wear-resistant materials with low friction for inertial instrument gas bearing use have been in development for about 10 years. Designs using monolithic, wear-resistant ceramic bearings have been, in general, replaced by those which attempt to surface-modify the basic structural material. As beryllium is commonly used in the fabrication of instruments, a beryllium composite gas bearing would have thermal and mechanical compatibility with the remainder of the instrument structure, as well as possess desirable wear performance at the bearing surface. Coatings on beryllium that have been developed and continue to be researched for further improvement include carbides, nitrides, and oxides which have been variously deposited by sputtering, evaporation, arc-plasma-spray, and electrodeposition. Several material and process options being used, together with their limitations are given in Table 1.

The present ONR program is designed to overcome the many processing problems and intrinsic difficulties encountered with coatings by means of an entirely different process that will alter the surface region of beryllium and impart the required wear characteristics to the material directly. The process is case hardening with boron by means of high temperature reactive diffusion of boron on a beryllium surface to form beryllium borides.

The attractive features of such a process would include:

(1) Enhancing surface coating integrity with a substrate by virtue of alloy formation between the coating material and substrate converting the base metal in situ.

Table 1. Materials and process options considered for bearing fabrication.

Material	Process	Problems Encountered
Solid Ceramic	Sintering and Hot Pressing	Difficult to Machine Physical Incompatibility with Instrument Design Requirements Low Thermal Expansion Poor Thermal Conductivity
Hard Coatings	Plasma Spraying (Thick)	Porosity, Adhesion, Cohesion, Plus Above
	Sputtering (Thin)	Adhesion, Composition, Structure, More Tolerable than Above because of Thinness of Coating
	Electrodeposition	Limited Maximum Hardness, Adhesion, Defects in Coating
Modified Surface	Case Hardening by Alloying of the Surface	None of the Above Perceived

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(2) Surface layer usually in slight compressive state which for hard, ceramic-type coating is desirable stress condition for strength and resistance to pull out.

(3) Typically slight dimensional change of part requiring minimal finishing to final dimensions; complex shapes can be coated uniformly; areas can be selectively stopped-off.

(4) Low cost, high reliability and producibility.

A review of the literature reveals only limited research has been conducted on the beryllium-boron system and little information on the formation of boride layers on various metals. A summary of the information on various beryllium borides is given in Table 2. The high values of microhardness of the boron-rich borides are very desirable for good

Table 2. Beryllium-boron binary system.

	BERYLLIUM	BERYLLIUM-RICH BORIDES		BORON-RICH BORIDES			BORON
COMPOUND	Be	Be_4B (δ)	Be_2B (α)	BeB_2 (β)	BeB_6 (γ)	BeB_{12}	B
METHOD OF PREPARATION		SINTERING HOT PRESS Be_4B	SINTERING	SINTERING Be_2B+Al	SINTERING		HALIDE THERMAL DECOMPOSITION
STRUCTURE DATA	HEXAGONAL	TETRAGONAL	CUBIC	HEXAGONAL	TETRAGONAL	TETRAGONAL	RHOMBOHEDRAL TETRAGONAL HEXAGONAL
ELECTRICAL RESISTIVITY	3.3×10^{-6} Ωcm	30×10^{-6} Ωcm	12×10^{-4} Ωcm	2×10^{-2} Ωcm	10×10^{6} Ωcm	60×10^{6} Ωcm	–
DENSITY (gm/cm^3)		1.96 1.92 2.01 THEO: 1.94	1.9	2.35 2.32 – 2.48	2.33 2.35	2.36	2.3 – 2.5
MICROHARDNESS	150-200 VHN	917 ±45 1350 KHN		3180 ±100 KHN	2577 ±75 KHN DROPS TO 2200 AFTER MELTING		2800 VHN
SOFTENING(S) AND/OR MELTING TEMPERATURES	1287°C	972 ±15°C	1450°C(S) INCONGRUENT MELTING	1700°C(S) NO MELTING WHEN HEATED TO 1970°C FOR 20 MINUTES	2020-2120°C CONGRUENT MELTING		2175°C
ENTHALPY OF FORMATION ΔH° (kcal/mol)		-18.3	-16.7	-15.5	-26.0	-38.6	

wear performance. Producing such phases in the surface of beryllium is the thrust of the present program. Several versions of the beryllium-boron phase diagram are shown in Figures 1, 2, and 3 and are the basis for predicting reaction compounds in our diffusion experiments since the structure of diffusion coatings should bear a direct relationship to the constitution of the corresponding alloy system. In the literature there is a degree of uncertainty in the exact compositions of several beryllium boride phases which we hope to clarify through results of this program.

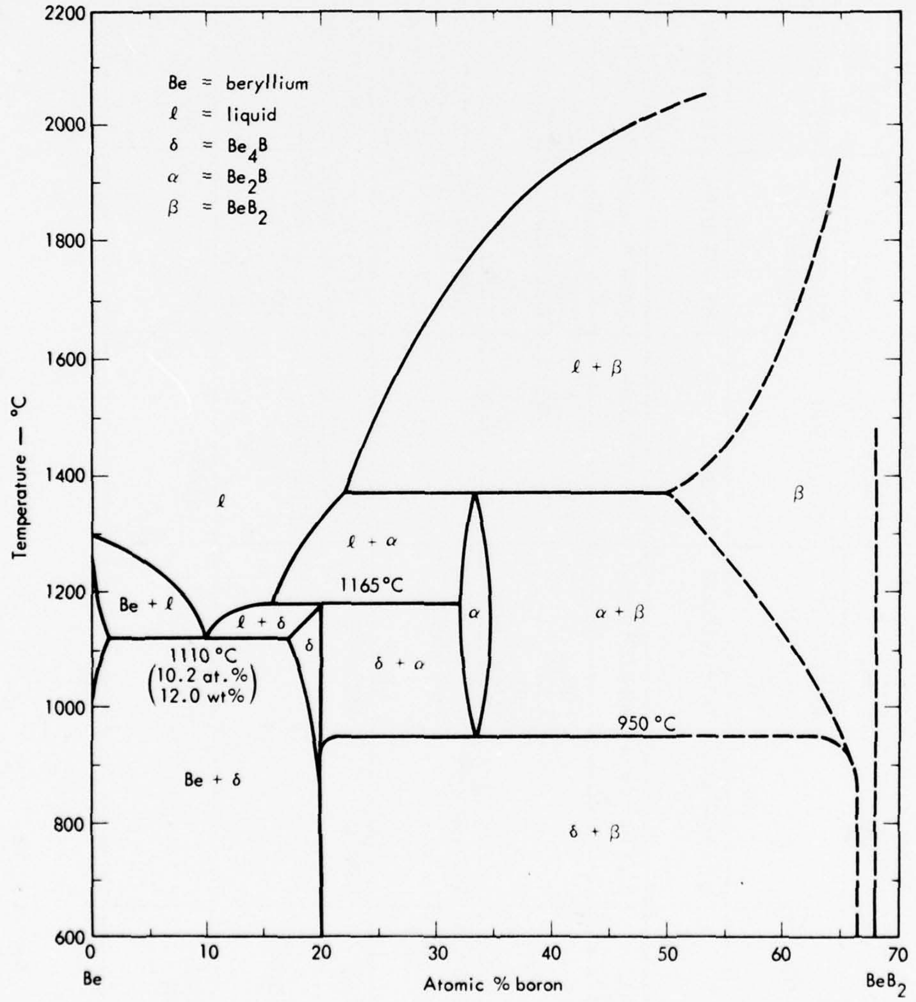


Figure 1. Be-B phase diagram (ORNL 1968; G. Godfrey, V. Frechette).

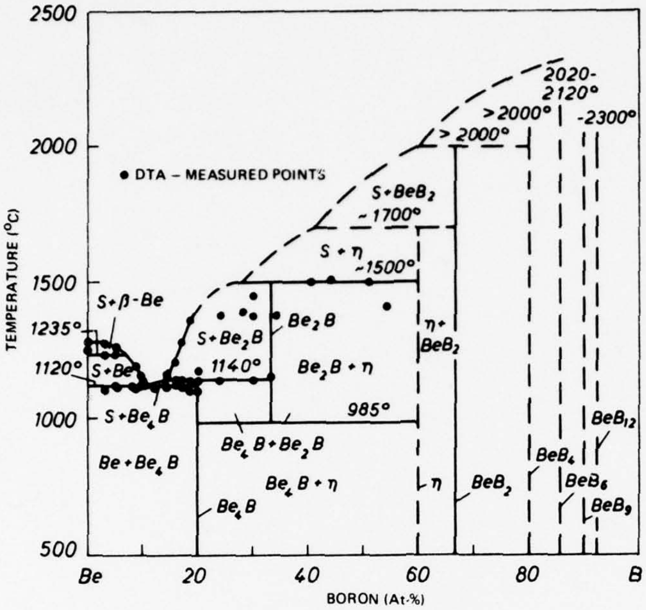


Figure 2. Be-B phase diagram (J. Stecher and F. Aldinger, Zeitshrift fur Metallkund, 64(10) 684-689 (October 1978)).

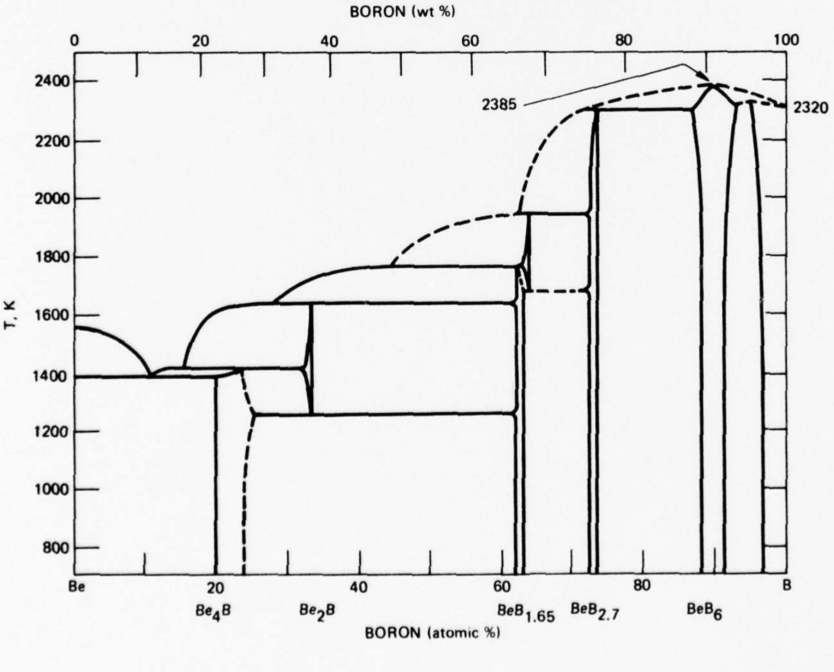


Figure 3. Be-B phase diagram (N. Stout, unpublished).

SECTION 2

OBJECTIVE

The objective of the present program is to surface-modify instrument-grade beryllium by solid-state reaction with boron to form beryllium boride. The resultant surface layer should have high hardness, good adhesion and low porosity, all of which are desirable characteristics of a precision gas-bearing material.

The kinetics of growth of the various intermetallics formed will be studied to expand the information available on this binary system and to allow process control of case thickness, composition, and structural integrity required for reliable performance.

SECTION 3

PROGRAM PLAN

The program plan has undergone some modification since the original program proposal. The objective of accomplishing the surface modification of beryllium by solid-sate case hardening with boron remains unchanged and is being pursued by several parallel approaches. The primary technique being evaluated is high temperature reactive diffusion of boron from solid and vapor sources into a beryllium substrate. In addition, we have added surface modification of beryllium by implantation of boron ions. The changes in the program plan have been in the following areas:

3.1 Diffusion Couples

Initial experiments with solid boron in the form of powder slurries and sputtered boron films reacted with beryllium at elevated temperature indicated a need for a more analyzable specimen configuration, namely a solid-solid diffusion couple to determine the kinetics and direction of intermetallic growth. These couples can be examined metallographically and allow diffusion directions and rates to be more conveniently determined.

3.2 Chemical Vapor Deposition of Boron

Attempts at getting boron from a vapor source available for reaction with a beryllium substrate are being considered. The two vapor sources of boron being examined are diborane and the boron halides.

3.3 Ion Implantation

Subsequent to the original program proposal, the ion implantation technique was explored and found to offer potential advantages (see Tables 3 and 4). This relatively lower temperature process is now being evaluated as a subtask in the program. The process of ion implantation involves essentially bombarding a surface with energetic ions from an ion accelerator to depths of about a micron in a controllable fashion. The limitation of the process at this time appears to be a rather low concentration of implanted atoms considered achievable using the present capabilities. The implantation experiments are being performed at NRL, which include implantation of boron into beryllium surfaces and analytical procedures to determine concentration and depth-profiles. Heat treatments and metallographic investigation of the implanted samples are being performed at CSDL.

Table 3. Advantages of ion implantation.

No sacrifice of bulk properties
Solid solubility limit can be exceeded
Alloy preparation independent of diffusion constants
No coating adhesion problems since there is no interface
No change in dimensions
Depth concentration distribution controllable
Composition may be changed without affecting grain sizes
Precise location of implanted area(s)

Table 4. Ion implantation parameters.

Implanted elements	-	Virtually any element from hydrogen to uranium can be implanted
Ion energies	-	Normally 2 to 200 KeV. Energies up to 5 MeV may be obtained with the Van De Graaff accelerator
Ion ranges	-	Vary with ion energy, ion species and host material. Ranges normally 0.01 μm to 1.0 μm
Range distribution	-	Approximately Gaussian. Choice of energies allow tailored depth distribution profiles
Concentration	-	From trace amounts up to 50 percent or more
Host material	-	Any solid material can be implanted
Special effects	-	Sputtering, radiation damage, radiation enhanced diffusion

SECTION 4

EXPERIMENTS

4.1 Evaluation of Deposition Methods

Various methods for introducing boron on a beryllium surface to produce intimate contact for reactive diffusion to take place include:

(1) Powder Pack
(2) Sputter Deposit
(3) Ion Plate
(4) Chemical Vapor Deposition
(5) Ion Implantation
(6) Molten Salt Bath
(7) Metalliding (Electrochemical Deposition in Molten Salt)
(8) Spark Deposition

It was felt that the least complicated and most contamination-free processes should be (1) direct combination of solid elements: boron from powder, sputter deposited and bulk material; and (2) boron deposition from a vapor phase. These processes also have the advantage of requiring easily available equipment. A third method, ion implantation, was decided to be a worthwhile technique to investigate since this process does not rely on classical diffusion mechanisms, solid solubility limits, or other parameters related to equilibrium conditions; also, since the process takes place at relatively low temperatures (below about 300°C), microstructural and topographical alteration of the substrate can be minimized.

4.2 Preparation of Test Samples

Instrument grade beryllium rod stock (Kawecki-Berylco HP-40 and Brush-Wellman I-400; nominally 4 percent BeO, Balance Be) was machined into flat disks (0.5-inch diameter, 0.25-inch thick) for both diffusion and ion implantation experiments. HIP-50 Be, with a lower oxide content and higher mechanical properties (and, therefore, a potentially superior gas bearing substrate), has been ordered and will be used in the later stages of the surface modification program with the most promising coating technique to emerge. Boron powders were bought as high purity grades, $>99^{+}\%$. Crystalline β rhombohedral was readily available (a stable form produced at temperatures $>1400^{\circ}C$; -60 mesh from Alpha Division Ventron Corp). Crystalline α rhombohedral (a form produced at temperatures $<1400^{\circ}C$ but will transform to β on heating $>1400^{\circ}C$) was not available from the commercial suppliers of boron contacted. Amorphous powder of <1 micron particle size was obtained from Fisher Scientific Corp. Crystalline boron rods (0.25-inch diameter) of better than five nines purity from United Mineral and Chemical Corp. were used for making diffusion couples.

4.3 Solid Boron Deposition

High purity amorphous boron and high temperature crystalline (β rhombohedral) boron were each mixed with amyl acetate to form powder slurries which were then painted on beryllium substrates (0.5-inch diameter flat disks) with a metallographic finish. The effect of beryllium surface finish (chemical etch, vapor blast, metallographic polish) was initially experimentally determined to be negligible with respect to slurry diffusion reaction rate.

Sputter deposited (0.5 and 1.0 micron thick) boron coatings resulted in smooth, adherent layers. Heavier layers of about 3 microns, were deposited by ion plating but gave non-adherent coatings, probably due to high residual stresses in the coating and therefore were not further used.

For the diffusion couples, solid rods (0.25-inch diameter, 0.4-inch long) of high purity crystalline boron and instrument grade beryllium were lapped flat and metallographically polished on the mating flat faces. They were assembled in a molybdenum fixture obtained from Manlabs, Inc., Cambridge, Massachusetts, and shown in Figure 4, that maintains intimate contact at the boron-beryllium interface during high temperature diffusion annealing by means of differential thermal expansion within the fixture.

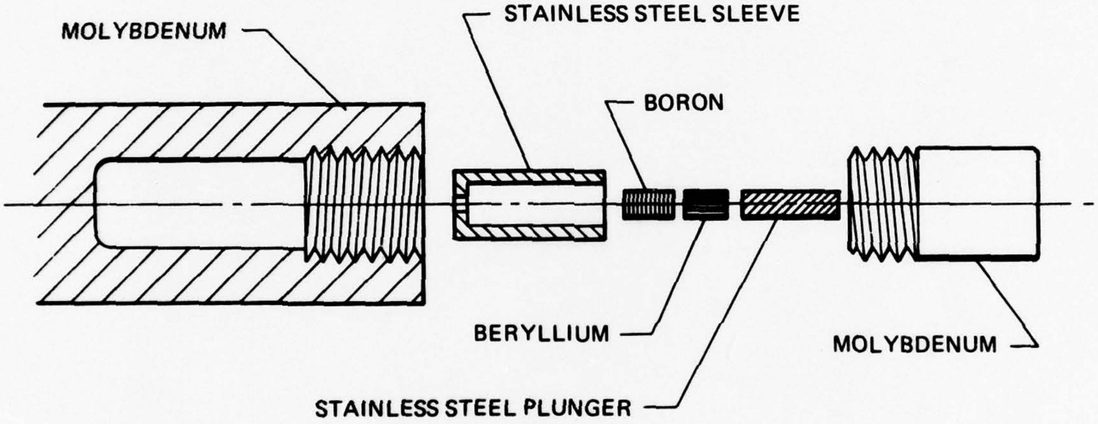


Figure 4. Diffusion couple fixture.

4.4 Diffusion Heat Treatment

A high purity vacuum/argon atmosphere, all-metal diffusion heat treating furnace was set up and the temperature profiled (see Figure 5). This system has been used for all solid boron to solid beryllium diffusion experiments with excellent results from a noncontamination standpoint. Argon was used as the heat treating atmosphere since it was found that at the diffusion temperatures used ($800^{0}C-1000^{0}C$) a moderate vacuum of 10^{-3} torr resulted in volatilization of beryllium. The following experiments were performed in this furnace:

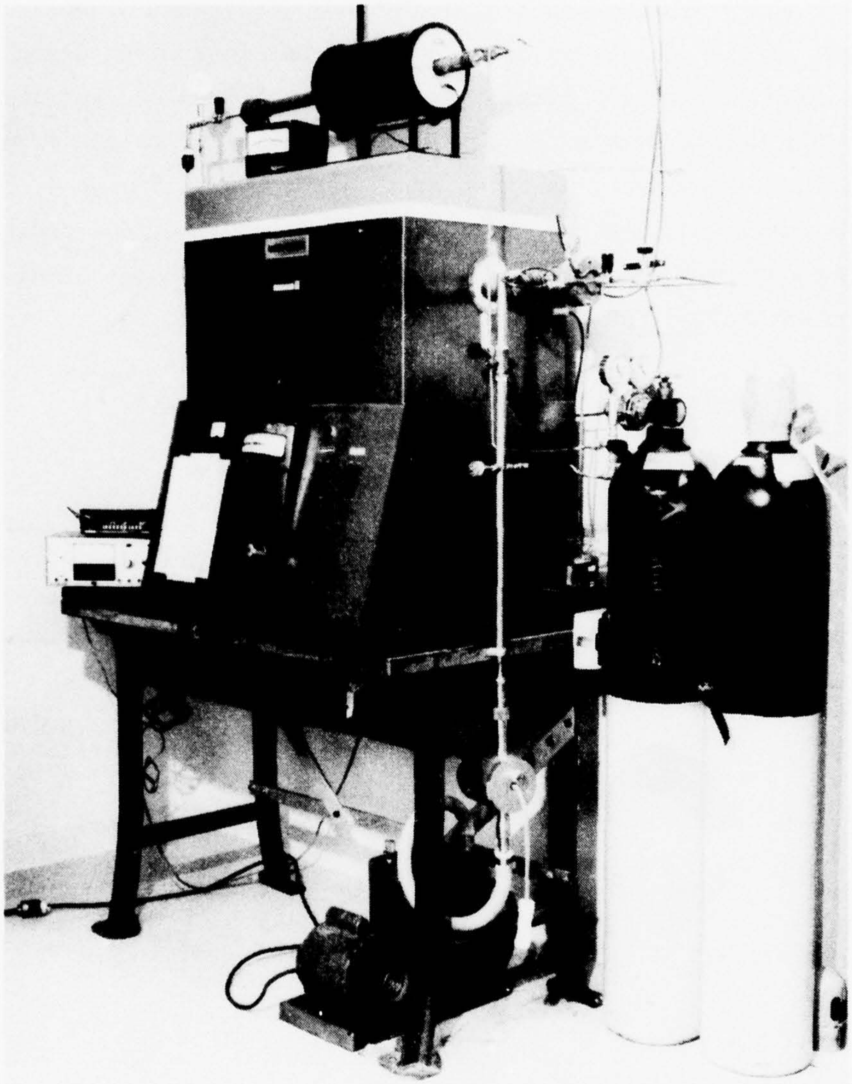


Figure 5. Diffusion heat treating facility.

(1) Amorphous boron and crystalline boron slurry coated beryllium test samples have been diffusion heat treated at 800°C, 900°C, 950°C, and 1000°C.

(2) Boron sputter coated samples have been diffusion heat treated at 900°C and 1000°C.

(3) Boron rod/beryllium rod diffusion couple assemblies have been treated at 900°C and 1000°C for up to 10 days at temperature.

Table 5 summarizes the results of experiments with diffusion couples.

Table 5. Experiments and observations of Be-B diffusion couples.

Run No. 1 900°C/8 hours/argon

No bonding

Boron cracked, spalled at edges; reaction indicated by ruby red areas on fracture surfaces

Beryllium has shallow crater where in contact with boron, rough surface; no color change

XPS and auger show no B on Be surface but Be on B surface

Run No. 2 900°C/10 days/argon

Same as above

Metallographic sections through interface show reaction phase adhering to B, none in Be. See Figure 6.

Chips of boron turned ruby red are undergoing X-ray diffraction

Run No. 3 900°C/24 hours/argon

Used copper plunger instead of stainless in fixture to reduce spalling due to excessive pressure - resulted in no spalling, no bonding

Color changes same as Run No. 1

Run No. 4 1000°C/10 days/ argon

No bonding

White deposit on both B and Be surfaces

Color changes same as Run No. 1

Couple surfaces undergoing X-ray diffraction to identify white deposit.

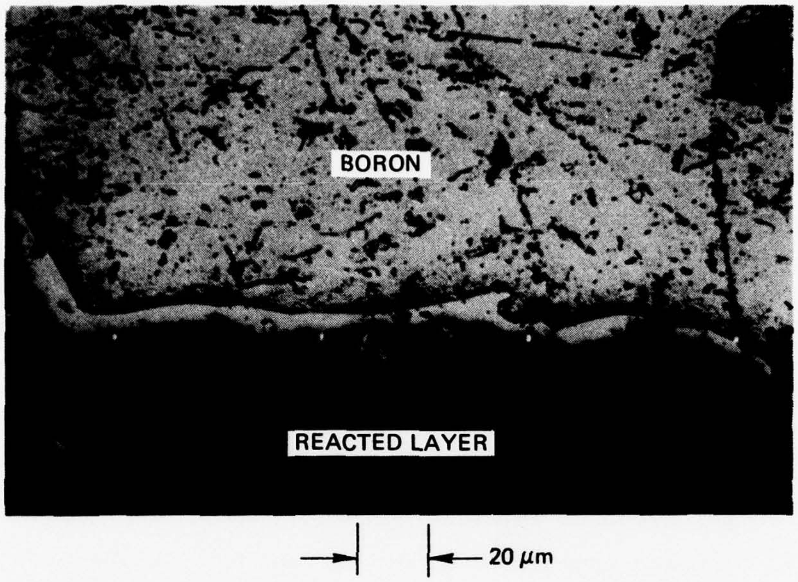


Figure 6. Metallographic section through boron sample after diffusion showing reaction layer at surface.

4.5 Ion Implantation

Ion implantation was performed on a one-square centimeter area in the center of a 0.5-inch diameter disk with four doses of successively higher implant energies (95, 140, 190, 250 KeV with a beam current of 10μa from a BF_3 ion source) in order to overlap the gaussian depth distributions of implanted boron atoms to maintain a uniform 10 atomic percent from the surface to a depth of about 8000 Å (0.8μ). The lateral uniformity was achieved by rastering the ion beam across the implant area. A macrophotograph of the sample is shown in Figure 7, and Figure 8 shows microphotographs of various regions of implanted area. The circular sample was quartered to produce 4 quadrant samples. One of the quarters was sent to NRL for Rutherford back scattering measurement to determine the thickness of the beryllium surface layer covering submerged boron implanted regions. The remaining quarters were used for heat treatments at 437 °C and 640 °C for 1 hour each. Hardness measurements were performed on these samples and are shown in Table 6.

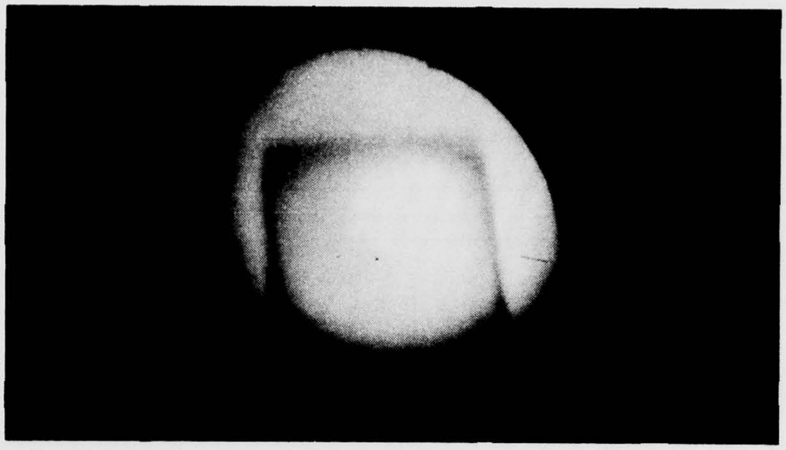


Figure 7. Macrophoto of as-implanted beryllium sample.

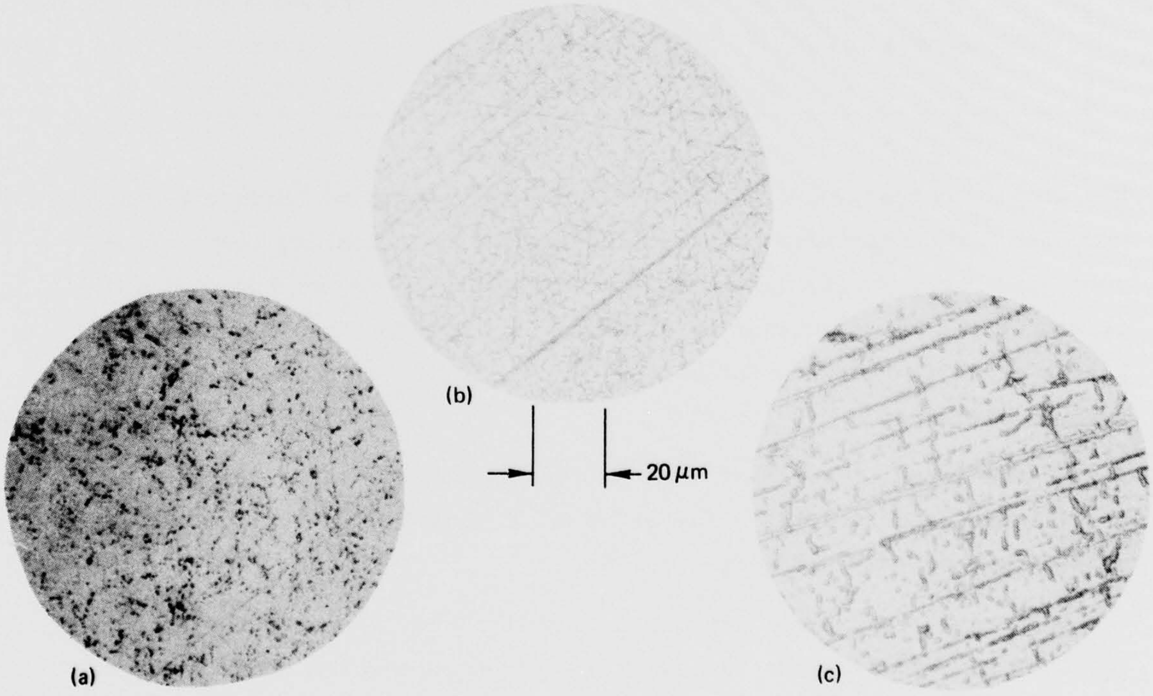


Figure 8. Metallographic views of various portions of implanted zone.

(a) Unimplanted surface with oxide inclusions.

(b) Fine precipitate or some new phases forming in area where not all doses overlapped.

(c) Coarse precipitate at the center of the implanted area where all doses overlapped.

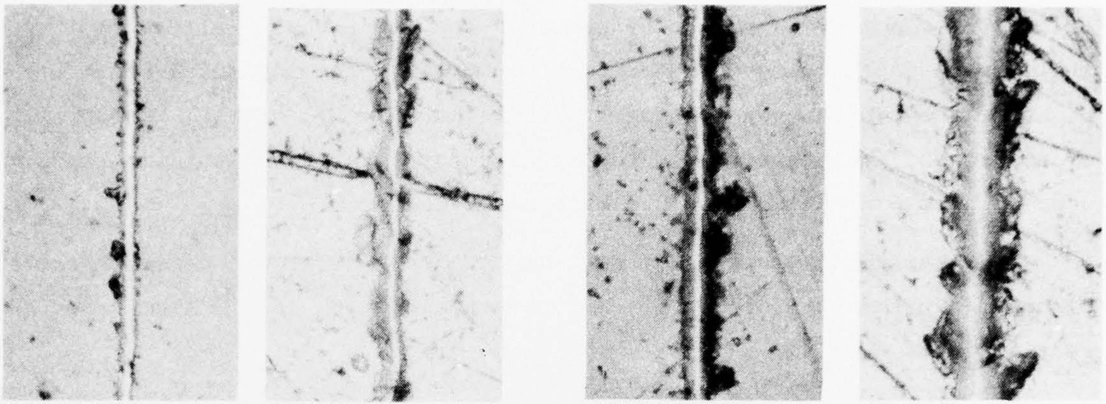
Table 6. Hardness measurements of 10% B implanted sample.

		Knoop Hardness Number	
	Load	Unmodified Area	Implanted Area
As Implanted	5 gm	493	947
	2 gm	566	1518
	1 gm	543	no impression
437°C Anneal	5 gm	462	1146
	2 gm	332	1833
	1 gm	241	no impression
650°C Anneal	5 gm	397	no impression
	2 gm	306	no impression
	1 gm	229	no impression

The data shows that for light loads (1 gm) the implanted surface was not indented whether annealed or not. Increasing the annealing temperature increased the capacity of the implanted surface to resist indentation. It is not yet known whether this is due to the layer itself getting harder or to its getting thicker by redistribution of boron atoms through diffusion.

The identification of a metallographic change (appearance of a precipitate) resulting from annealing boron implanted beryllium is being carried out by TEM diffraction method.

Scratch tests were performed on both implanted and unimplanted areas of as-implanted and variously heat treated samples under loads of 3 and 9 grams (see Figure 9). The results of scratch tests confirm the fact that the implanted areas have higher hardness than the unimplanted areas. Unexpectedly, scratch tests performed on heat treated surfaces of implanted specimens did not follow the trends observed by microhardness measurements, i.e., higher hardness with higher annealing tempera-

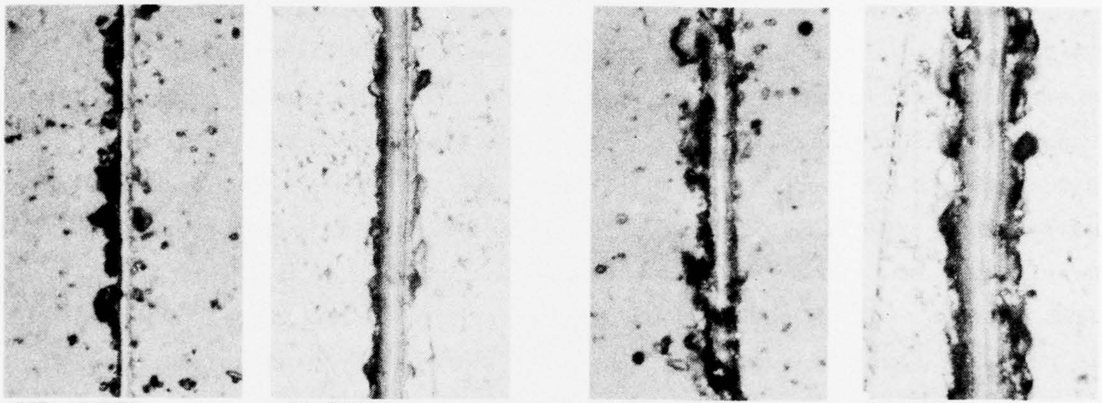


IMPLANTED ORIGINAL

3 gm LOAD AS IMPLANTED

IMPLANTED ORIGINAL

9 gm LOAD AS IMPLANTED

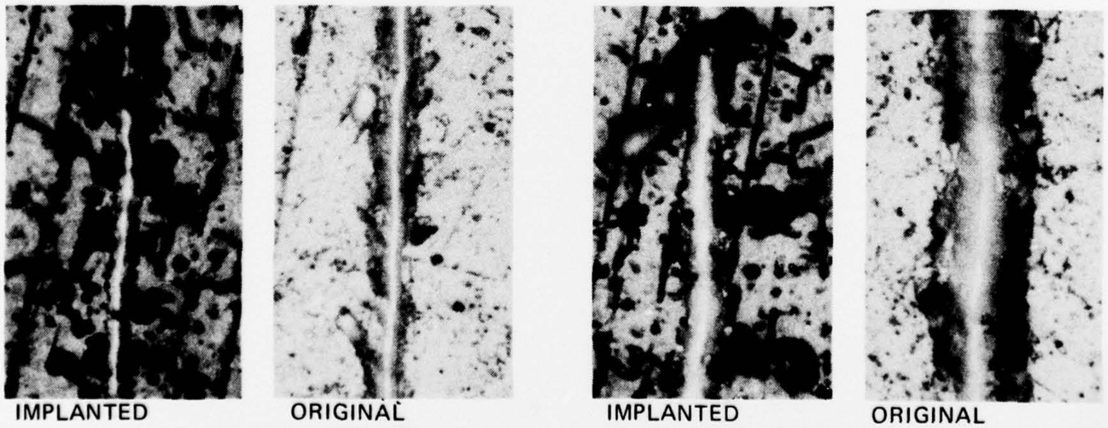


IMPLANTED ORIGINAL

3 gm LOAD AFTER 437°C

IMPLANTED ORIGINAL

9 gm LOAD AFTER 437°C



IMPLANTED ORIGINAL

3 gm LOAD AFTER 650°C

IMPLANTED ORIGINAL

9 gm LOAD AFTER 650°C

10 µm

Figure 9. Scratch test appearance on implanted and unimplanted beryllium

ture. This anomaly is yet to be resolved but is probably related to the scratch depth being of the order of 800 times the implanted depth of about one micron even for the lightest load used (3 grams). Knoop microhardness indentations, on the other hand, even at the maximum load used (5 grams) are typically 0.5 micron or less deep.

Higher concentrations of implanted boron (>30 atomic percent) are planned. Further improvement in hardness compared to the 10 atomic percent boron is expected.

4.6 Chemical Vapor Deposition

Preliminary experiments have been made in reacting boron as it is being vapor deposited on an induction heated beryllium specimen in a glass chamber under flowing argon atmosphere. The source of boron vapor was a commercial boriding pack cementation compound containing B_4C (active boron source), SiC (filler), and KF (energizer), induction heated in a graphite susceptor close to the beryllium substrate. Beryllium surface reaction products are being analyzed by Auger and SIMS methods. It is not yeat clear whether the surface layer produced is pure boron or a Be-B compound, but the coating is adherent in contrast to the reaction compounds resulting from solid beryllium - boron interactions, which separate easily from the beryllium substrate.

SECTION 5

ANALYSIS AND EVALUATION

Most of the current effort is in the area of analysis and evaluation of diffusion and implantation experiments already performed.

5.1 Analysis

The following is a description of the analytical methods being used.

(1) *Metallography of heat treat specimens* is being done using a beryllium metallographic facility set up for this program with arrangements for handling toxic dust-producing operations (see Figure 10). A technique for specimen edge retention by means of filled mounting compound is being used to observe the thin layers produced. Several etchants for delineating microstructure have been developed.

(2) Knoop microhardness testing of thin reaction zones is being done using loads down to the practical limit of this method, i.e., in the range of 1 to 10 grams. Hardness data must take into account the influence of such light loads on results and therefore hardness numbers may not be directly compared to published values of other materials.

(3) Scratch hardness testing capability has been set up at CSDL. This is fairly unique since attempts to locate such a capability at several educational and research establishments in this area were not successful. A Bierbaum microcharacter scratch apparatus was obtained

and upgraded with a new diamond stylus. This tool is very useful for characterizing hardness and adhesion of thin films at light loads. Tests have been done on boron implanted specimens with standard loads of 3 and 9 grams. Testing at lighter loads will also be explored.

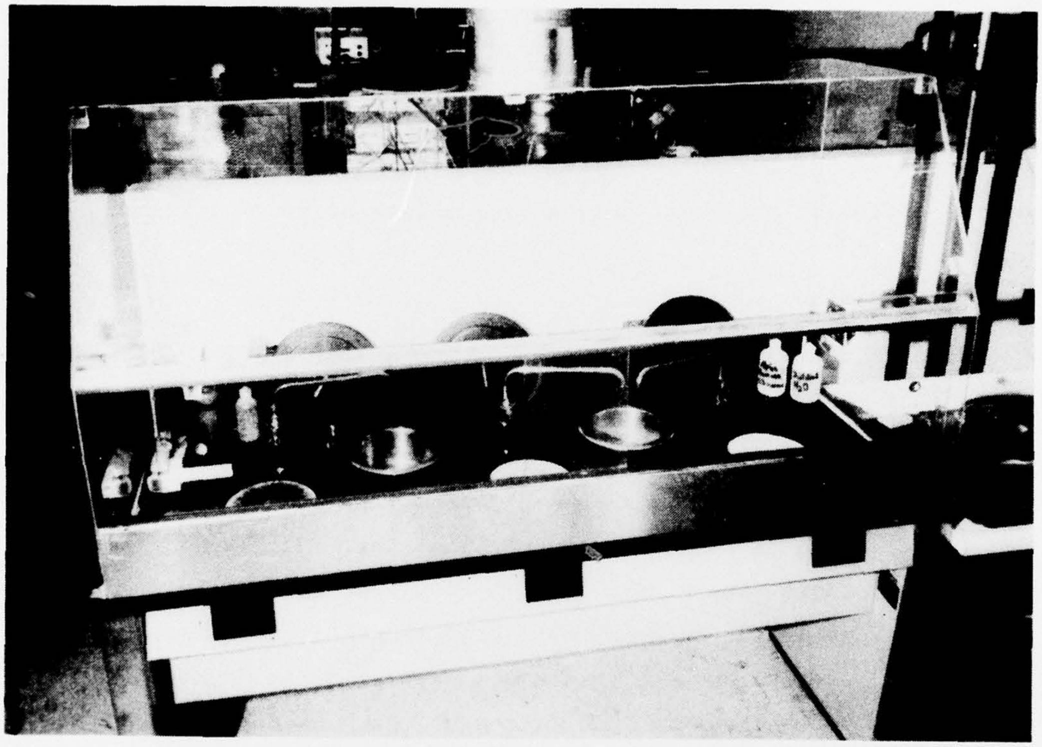


Figure 10. Beryllium metallographic facility.

(4) Debye - Scherrer x-ray diffraction of powder samples of beryllium and boron reaction products after diffusion heat treatments has been done. Samples of various commercially prepared beryllium boride powders are also being x-rayed for use as standards and aiding in interpreting the complex patterns so far obtained.

(5) Because of the low atomic numbers of beryllium and boron, the more familiar analytical tools of energy dispersive x-ray analysis and electron microprobe are not feasible. Because of the thinness and possible multiple composition of reaction products, standard or low angle x-ray diffraction of test specimen surfaces is not feasible. Techniques to overcome these probelms are Auger Electron Spectroscopy (AES), Secondary Ion Mass Spectroscopy (SIMS and Transmission Electron Microscopy/Diffraction (TEM). Facilities capable of handling beryllium specimens have been located and have started analyzing powder beryllium boride standards.

5.2 Evaluation

Initial results after diffusion heat treatment with solid beryllium in contact with various forms of solid boron indicate a greater tendency of the beryllium to enter the boron structure than vice-versa. Since there is no mutual solubility of these elements as evidenced from the phase diagram, a compound must form immediately at their interface, and rates of diffusion of the elements through the compound will determine the direction of compound growth. Further metallographic studies of diffusion couples run at different temperatures and times will establish the kinetics of compound growth and the information necessary to control its development. While at this point, the metallographic evidence is of compound growth into the boron, it is not yet certain whether this is a fundamental atomic diffusivity phenomenon or a consequence of the particular materials and mating conditions used, for example, the presence of contaminating films at the interfaces or the crystallographic form of boron. Other evidence of boride formation in the boron rather than in the beryllium substrate were color changes on boron surfaces, porous zones between the beryllium and the as-yet unidentified compound in the boron, and no trace of boron being picked up by Auger Electron Spectroscopy on the separated beryllium side of diffusion couples. Further diffusions under different controlled conditions will hopefully resolve the diffusion direction question.

It is felt that introducing boron atoms to the beryllium solid from a vapor phase rather than from a boron solid could give different diffusion results since conditions at a surface where one component is condensing are quite different from those at an interface between solid diffusing materials. Such a process could also control the concentration of boron atoms free to react with the beryllium to give beryllium-rich borides. This seems to be indicated in preliminary experiments with CVD of boron on heated beryllium substrates. This resulted in a hard adherent surface layer with perhaps a coefficient of thermal expansion more compatible with the beryllium substrate than that of compounds obtained from solid boron sources which separated from the beryllium. This will receive further analysis. The use of glow discharge assisted CVD to deposit boron ions could enhance the driving force for diffusion of the boron, that is, the concentration of boron atoms in the beryllium surface, by overcoming surface contamination effects. This process has been reported to be successful in greatly increasing the nitriding and carburizing of various metals.

If, in fact, the diffusion system of Be-B can not be modified to allow boriding of beryllium rather than berylliding of boron, the ion implantation technique will take on added significance since this process is not diffusion dependent. The results to date have shown the feasibility of implanting in beryllium to depths of about a micron low concentrations (10 atomic percent) of boron with minimum surface damage and measurable, significant improvement in hardness and scratch resistance. By the Rutherford backscattering technique, it was shown that implanted boron can be made to move through the unmodified beryllium lattice by thermal anneals as low as $400^{\circ}C$. What appear to be fine precipitates of as yet unknown composition have been observed in specimens annealed at temperatures of $450^{\circ}C$ and coarse precipitates at $600^{\circ}C$. Identification of this reaction is being done by TEM diffraction.

The maximum concentration of implanted atoms is limited by the sputtering rate of the substrate during the ion bombardment. Since it was experimentally determined that beryllium has an extremely low sputtering coefficient during boron implantation, there is an excellent prospect of achieving high boron concentrations (>50 atomic percent) in a beryllium surface layer. This will be attempted in the near future. A further improvement in hardness properties is expected as well as enhancing the conditions for forming high boron-containing borides.

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