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for  
CRADA Number ORNL 04-66845

Between

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and

Brontek Delta Corporation  
(Participant)

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For the Participant

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July 29, 2004  
(Date)

1 Contract No. N00178-03-C-3142

Beryllium Smoothing

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Final Draft

*Final Report*

**Smoothing of Military Mirrors by a Novel Surface Alloying  
and Melting Technique<sup>1</sup>**

Prepared for

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implanted sample, the first boron sample and two control samples have been heated to 800 C in this IR system. This program could not obtain sufficient priority on the IR furnace to make adequate progress, however. Therefore, another system was constructed by BronteK personnel, using components largely borrowed from ORNL. This system and results will be described. Heating by use of this latter system has proceeded to as high as 1160 C.

- **Results, Conclusions and Discussion:** The main result is that, despite apparently having heated samples to as high as 1160 C in the new system, melting has apparently not yet occurred. The as-machined texture is still visible in the microscope. The reasons will be discussed.

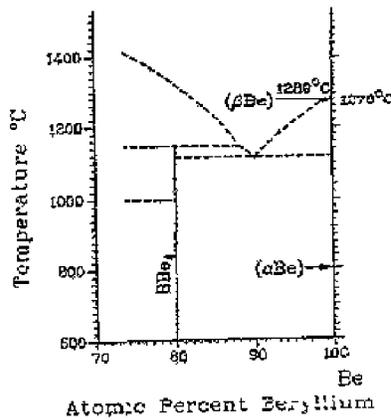


Fig. 1: Binary phase diagram for boron-beryllium showing the beryllium-rich region.

### Samples

Sixteen samples were selected from materials that had been used in a previous optical program at Oak Ridge National Laboratory. In addition, a spare accelerator window was considered as a possible candidate because of the large, thin area presented and the potentially usefulness for making several ion implantation samples. The 16 samples were generally coupons of about 4 cm diameter and 1 cm thickness. They were physically measured with machinists measuring instruments and weighed for determination of

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## Beryllium Smoothing

**Table 1 Physical measurements of the seventeen samples**

26-Oct-03

Densities of beryllium samples, ideal = 1.848 g/cm<sup>3</sup>

Sample #	Diameter (cm)	Thickness (cm)	Volume <sup>1st</sup> approx (cm <sup>3</sup> )	Volume correction (cm <sup>3</sup> )	Volume Final (cm <sup>3</sup> )	Mass (g)	Density (g/cm <sup>3</sup> )
OR-1	4.066	1.465	19.02225	0.021775	19.00048	34.3486	1.807776
OR-2	4.004	1.504	18.93762	0.021775	18.91585	34.9714	1.848788
OR-3	4.008	1.504	18.97648	0.021775	18.95371	35.04965	1.849224
PE-001	5.081	0.64	12.97681	0	12.97681	23.79742	1.833842
PE-002	3.79	0.997	11.24768	0.038927	11.20876	20.66925	1.844027
PE-003	3.802	0.994	11.28496	0.039052	11.24591	20.70499	1.841113
PE-004	3.789	1.002	11.29813	0.038917	11.25921	20.74053	1.842095
R1	3.808	1.014	11.54839	0	11.54839	21.50979	1.86258
window	10.17	0.079	6.417391	0	6.417391	11.50293	1.792462
OR-4	4.006	0.982	12.37721	0.021775	12.35544	22.7924	1.844726
OR-5	4.001	0.982	12.34634	0.021775	12.32456	22.7434	1.845872
OR-6	4.01	1.025	12.945	0.021775	12.92323	23.6995	1.833869
OR-7	3.995	0.98	12.28426	0.021775	12.26249	22.6282	1.845319
OR-8	4.006	0.988	12.38982	0.021775	12.36804	22.8036	1.843752
OR-9	4.008	0.981	12.37696	0.021775	12.35516	22.7785	1.843639
OR-10	4.007	0.982	12.36339	0.021775	12.36162	22.8015	1.84454
OR-11	4	0.982	12.34017	0.021775	12.31839	22.8191	1.852442

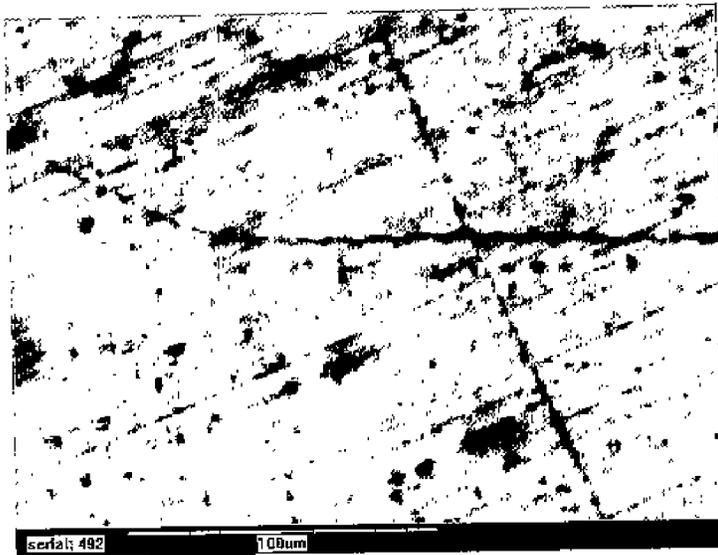


Figure 4: Optical micrograph of sample OR-5 at the magnification indicated. The machining texture due to tool advance is clear.

Figure 4 is an optical micrograph showing the as-machined texture of the sample surface for OR-5. Results for sample OR-4 are the same. The machining texture is evident.

### ***Ion implantations***

Originally it was planned to carry out the ion implantation work and RBS measurements using the facilities of the STTR partner, the Oak Ridge National Laboratory (ORNL). After the award announcement, ORNL shut down its accelerator facilities and also the furnace equipment we were planning to use. It was decided that ORNL would continue as the STTR partner by providing the safety oversight and different heating equipment, while the ion implantation work and RBS measurements would be moved to the Alabama A & M Research Institute (AAMURI) at Normal, AL (near Huntsville). For the AAMURI, a subcontract was let, and the amount originally planned for the STTR partner was reduced from half of the total award to about 35 %. The situation at AAMURI was that the tandem accelerator, which provided high energy ions for the RBS, was a mature

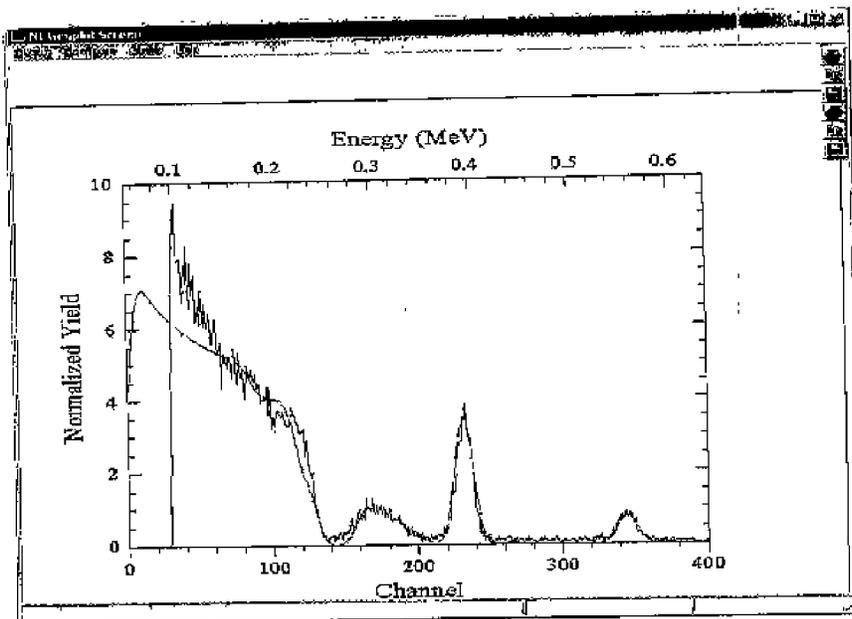


Figure 5: RBS histogram of first material ion implanted with boron. This analysis illustrates the problem with carbon incorporated adventitiously. The large carbon peak centered at approximately Channel 230 (0.38 MeV). The implanted B is a broader peak just below the carbon peak.

As a result of these modifications it has been possible to implant three samples with boron and maintain excellent cleanliness of the surface. That means both in terms of visual appearance and objective analysis as well. Figure 9 is an RBS histogram for one of the last three samples implanted. It is clear that the carbon peak is much improved relative to that of Figure 5, although quantitatively, there is some slight increase in both the O peak and the C peak due to the implantation. The boron content is somewhat over 10 % over a depth of about 100 nm. Therefore, this sample (and the other 3) represent very satisfactory results. In addition, the surface is indistinguishable from the unimplanted to the naked eye.

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Beryllium Smoothing



**Figure 7: Photograph of tilt-rotation sample manipulator used for ion implantation of Be samples without the shroud. The boom is insulated and the drive chain has an insulated sprocket, so that beam can be integrated from the electrically isolated sample mount.**

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Table 2: Concentration versus depth parameters for RBS analyses of boron-implanted Be done at AAMURI. There are ten layers reaching to a depth of about 200 nm total and then the substrate is solid Be. For the thickness of each layer of 200 "units," a unit is  $10^{15}$  atoms/cm<sup>2</sup>, in the nuclear units needed for analysis. Somewhat fortuitously, each of these units is a thickness of about 0.1 nm or 1 angstrom. Therefore the thickness of each layer is 20 nm.

Layer	Thickness	Sublayers	Composition
1	200 00	CM2	auto C 18 000 Be 76 000
2	200 00	CM2	auto C 2 000 Be 98 000
3	200 00	CM2	auto C 2 000 Be 98 000
4	200 00	CM2	auto C 4 000 Be 96 000
5	200 00	CM2	auto Be 98 000
6	200 00	CM2	auto Be 98 000
7	200 00	CM2	auto Be 98 000
8	200 00	CM2	auto Be 98 000
9	200 00	CM2	auto Be 98 000
10	200 00	CM2	auto Be 98 000
11	10000 00	CM2	auto Be 1 000

SIMS File	A 5940 new
Identifiler	
EDT Term	Composition date 1024 Digital offset 0
Date	FEM 01 2004
Beam	1 500 keV 4mm 100 00 ucmnt e 36 00 e4
Geometry	180 Theta 0 00 Phi 10 00 Psi 0 00
MCA	Range 1 440 20 000 First chnn 0 0 NPT 1024
Detection	FOEM 18 0 keV Top 1 0 Gains 0 275
Correction	1 0000
Up portscope	1

Altogether five samples were implanted. Two with the adventitious carbon and three under the clean conditions. Three of a total of eight were used for controls to study heating results.

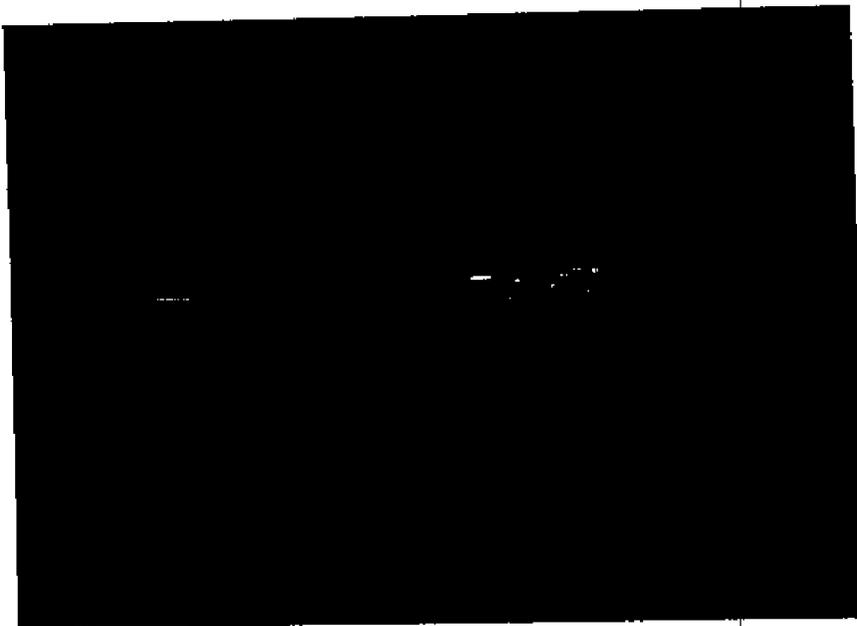


Figure 10: Photograph of the B ion implanted sample as encapsulated in quartz for heating. The sample has been heated to 800 C for one minute.

Before sealing, the capsule was evacuated and flushed with argon several times, and then backfilled with a gas mixture consisting of 1 % O<sub>2</sub> and 99 % Ar. The principal reason for the cover gas in general was to help reflect any possible evaporating atoms back into the surface, and thus reduce the evaporation rate, if any. The O<sub>2</sub> gas was added at a level which might, in principle, react the adventitious carbon for these particular samples. This latter hope was speculative and somewhat of a long shot given that the free energy of formation of B<sub>2</sub>O is much lower than that of CO<sub>2</sub> or CO (algebraically). However, there might be some reason to hope that the carbon is nearer the surface and not as well passivated as the average B atom. In any event, the O<sub>2</sub> was added. One control sample had the added O<sub>2</sub> and one had only pure Ar.

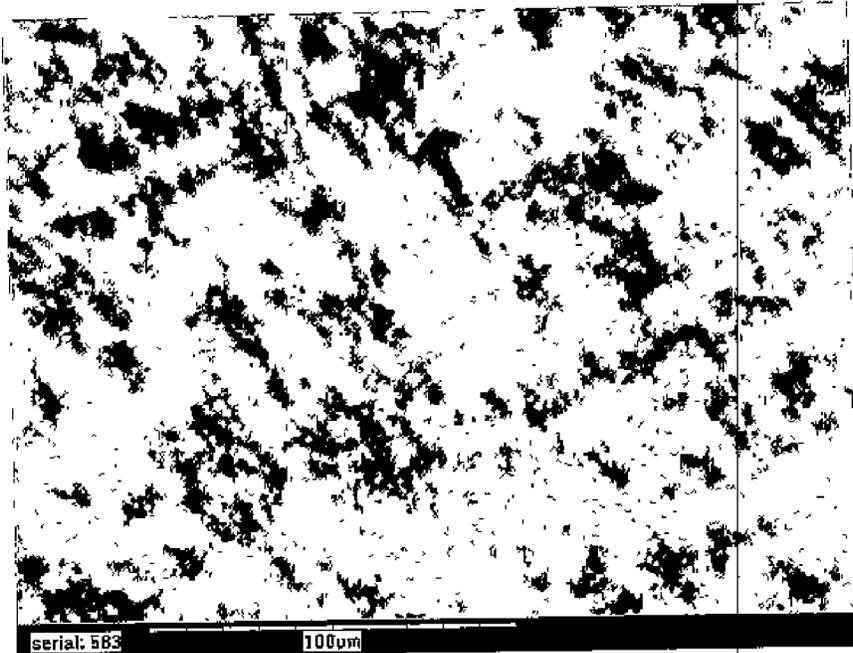


Figure 12: Optical micrograph of boron-implanted sample after heating to 800 C. Compare with Figure 4, which shows the as-machined texture.

apparent oxidation of both control samples. The reason is not known. Thermodynamically, Be reduces  $\text{SiO}_2$  with the ease, but at 800 C, the absolute vapor pressure of  $\text{O}_2$  over  $\text{SiO}_2$  is only  $10^{-33}$  atmospheres (or about the same as we stated above for BeO at 1200 C). Thus, the calculated absolute evaporation rate of  $\text{O}_2$  from  $\text{SiO}_2$  could not have produced enough  $\text{O}_2$  to have tarnished the sample. Moreover, the sample is doubly contained anyway. For heating, the capsule was placed in another quartz sleeve in the furnace, through which Ar gas was flowing on the outside of the capsules. Therefore diffusion of oxygen through the quartz would not appear to be a ready explanation. Argon typically has about 100 ppm of oxygen impurity unless specially specified, but we added 1 % to one of the capsules anyway. Thus the inventory of  $\text{O}_2$  trapped in the capsule would not have appeared to have been enough to have tarnished the sample for the nominally pure Ar. In addition, there was little difference between the one containing deliberately introduced.

At present the somewhat tarnished, and probably unacceptably tarnished, control samples remain in their capsules. The N-implanted and B-implanted samples appeared more heavily tarnished. They were removed and inspected by microscopy and profilometry.

A drastic change has occurred for the B implanted sample, but it is not smoothing, and the change may not be related to oxidation. The sample surface has roughened considerably. The as-machined texture has been completely obscured, and replaced by another topography.

Figure 11 shows the profilometer trace for the B-implanted sample and Figure 12 shows the optical micrograph. For the trace, the  $R_A$  value has gone from 25.5 nm (Figure 3 e.g.) to 165 nm, a depth comparable to the ion range. Figure 12 is the optical micrograph, and again, there is obviously no connection to Figure 4.

These results illustrate the reasons for observing the evolution of the texture through a stepwise heating schedule. The ultimate effect of heating to the planned temperature can not yet be predicted. A large effect is occurring.

The "Brontek" system was rapidly constructed in order to obtain a dedicated system for better progress. The system also provided for different features and an environment with more readily variable parameters than the ORNL system. The system provided for a flow-through of the environment and cover gas at any pressure from about 1 micorr to one atmosphere. Provision was made for pumping and purging several times before introduction of the flowing cover gas. The only gas that was actually used was "forming gas," a mixture of 4 % H and 96 % Ar. The heater was a boron nitride heater capable of about 1300 C at 110 V, the highest voltage that was used. Because of the thickness of the samples, 1 cm, it was expected that the gradient from bottom to top in the samples might be considerable. To mitigate this factor, a system of tantalum radiation shields was constructed for the cylinder wall of the sample. The area of the heater not covered by the sample was also heat radiation shielded. Temperature of the surface was measured by a thermocouple held to the edge of the top sample surface by the top radiation shield, which also served as a sample retainer, and was secured tightly. Provision was made for

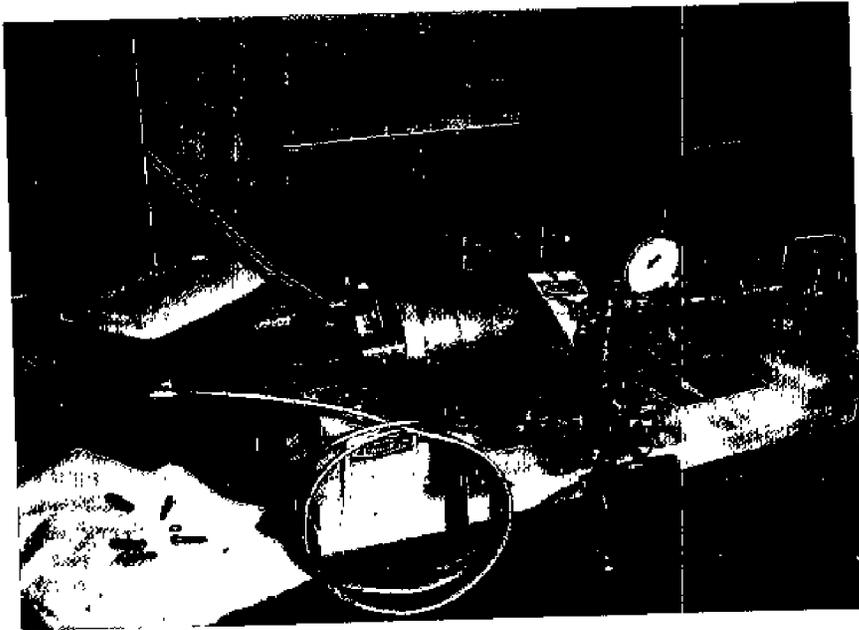


Figure 14: Photograph of the chamber part of the Brontek heating system. Gas supply control valves and pumping system, which enable rather precise control of the flow-through atmosphere are not shown.

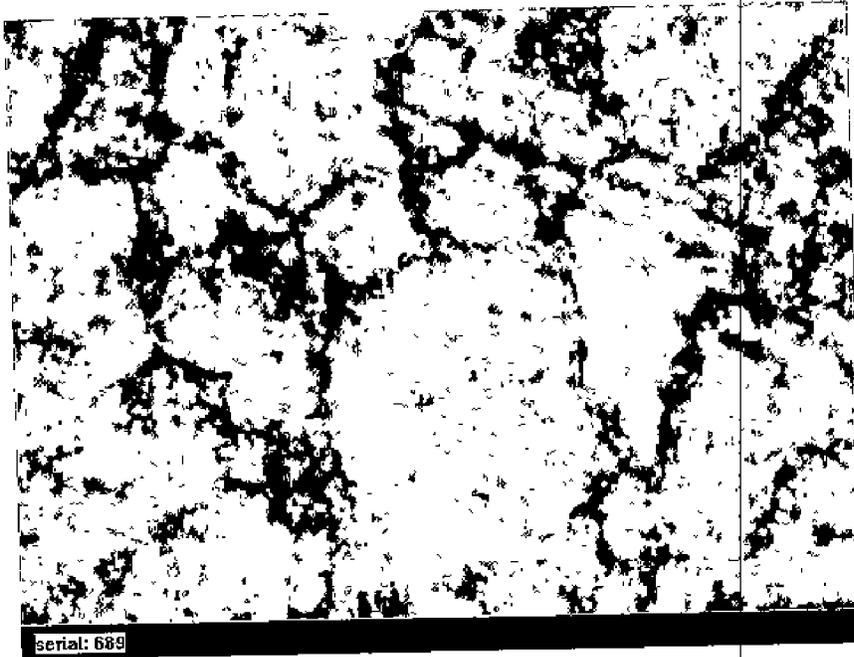


Figure 15: Micrograph (200 X) of sample 5-4 after heating to 1170 C.

**Conclusion:**

The overall conclusion is that the main hypothesis of the proposal was neither proved nor disproved. Further advancement will depend on development of a heating technique that will allow heating to the melting point with surface cleanliness. If this can be done by use of a suitable atmosphere or by a gettering technique (hot calcium e. g.) then the process will be commercially viable. If it requires ultra high vacuum techniques, the process may not be commercially viable.

and fully functioning facility. However, the low energy ion implantation facility was newly installed, not fully shaken out and was a work in progress. As a result, a great effort has gone into further refinement of the latter facility for these experiments. There were several issues as regards strength of beam, ion dosimetry and other factors, and all issues are interconnected. One problem that had a lot to do with the result, in conjunction with a fairly low dose rate, was apparently fairly poor vacuum in the target chamber. As a result, samples became visibly discolored due to carbon contamination during the implantation. Carbonaceous gases deposited on the surface or near the surface are decomposed by the beam to leave carbon. Figure 5 is an RBS histogram which indicates the presence of carbon. In Figure 5, the rather broad peak due to implanted boron is clear at just below the carbon peak. The carbon peak is oversized and may be compared with that of virgin materials, as shown in Figure 1. There is also some increase in oxide thickness as well, due to the implant. Two ion implants, the one represented in Figure 5, and one involving implantation of nitrogen atoms were performed in the chamber in this configuration.

Although RBS analysis results may be interpreted by either deductive or forward analysis as compared with inductive or simulation by theory, the theory of the analysis is in such excellent shape that analysis is usually by the latter approach nowadays. The red curve in Figure 5 is for a simulation using the energy of the incident He ions, other spectrometer parameters, and the concentration profile given in Table 2. The boron implant is not exactly what was intended but is close enough to warrant continuing with the intended heating. The average boron concentration is some 12 at % over a range of 40 to 180 nm, but the total dose is almost precisely what is measured by the dosimetry, based on integration of ion current applied to the sample. This latter result has been general.

Owing to the undesirable results regarding carbon, however, it was decided to rebuild the target chamber to provide for better pumping. An ion implantation chamber that had been in use as part of the ORNL facility was borrowed and installed.

This work required a week of labor for Brontek and AAMURI personnel. The chamber added one new pump to the system, a clean roughing system, and a liquid-nitrogen cooled trap. Figure 6 is a photograph of the new installation with instrumentation, as it terminates the beam line. The implant accelerator itself is out of the picture on the left.

Ion implantations are performed in the front port by use of a "tilt-rotation" manipulator, which also provides for electrical isolation and beam pick-up. There is also a dual purpose shroud, which by polarization, improves dosimetry by suppression of secondary and tramp electrons. The shroud is of solid rather than grid form to allow for capture of any sputtered Be atoms. It is lined with Al foil, which can be removed and analysed for any sputtered Be and then disposed off. Figures 7 and 8 are photographs of the manipulator with and without the shroud.

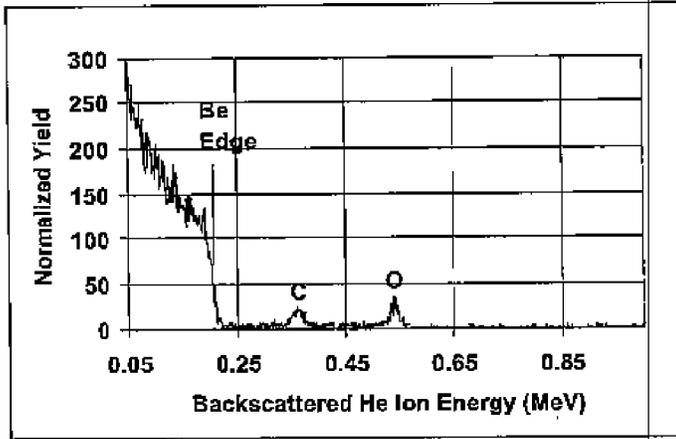


Figure 2: RBS analysis for unimplanted Be coupon. 1.6 MeV He ions in 170 deg backscattering angle.

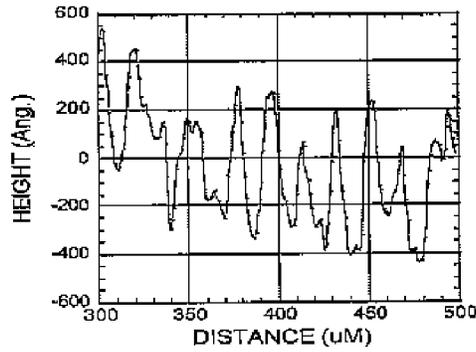


Figure 3: Portion of profilometer trace showing as-machined texture. The trace direction is radial. The tool advance is about 20  $\mu\text{m}$ . The smoothness for a machined surface is very good with an  $R_a$  of value of 25.5 nm for a trace of 1 mm length.

density. In general, the densities appeared to be near ideal (Table 1), and there was no reason to expect much void space due to sintering. Small corrections in the volume were due to beveled edges and the like. The uniformity in density among the samples provided some confidence that most of the materials were probably satisfactory.

Machined samples had regular turning textures, where the spiral texture due to tool advance was evident. These topographies were studied by profilometry and by optical microscopy for ideality and suitability for ion implantation, in terms of relationship of the topography to ion range. Also, the purity of the samples was ascertained by use of RBS.

Samples OR-4 and OR-5 were selected as the best for the Phase I program on all counts, and they were virtually identical. After selection, each was sectored into four quarters by procurement from a beryllium-qualified shop.

Figure 2 shows an RBS histogram for OR-5. The data are the same as for OR-4. The peaks at about 0.36 and 0.49 MeV are for surface carbon and surface oxide on the Be. These contaminants are perfectly normal at the levels shown for material that has been polished or machined and exposed to air for a time. A full quantitative analysis has not been done, but it can be estimated from experience that the amount of carbon or oxygen is about ten atomic layers of each. The very low background at all other energies means that this material is as pure as any ever seen by the author. Quantification would depend on assuming some particular impurities (with no particular ones having been detected) and then doing a simulation. There would be less than 100 ppm of impurities in the midrange of atomic masses, copper e.g.

Figure 3 is a profilometer trace, fully representative of the prevailing machining texture for samples OR-4 and OR-5. The regular waviness due to the tool advance upon turning is completely evident, with the tool advance being some 20  $\mu\text{m}$ . The vertical axis has a range of only about 120 nm, and the arithmetic average roughness,  $R_A$ , was only 25.5 nm for this trace. For all traces on samples OR-4 and OR-5 the  $R_A$  value was in the low to mid tens of nm.

## ***Introduction and Summary***

### **Concept of Program:**

This report will summarize the tasking and results to date of the subject program on "Smoothing of Military Mirrors by a Novel Surface Alloying and Melting Technique"

The idea of the program is to utilize the equilibrium chemistry between boron and beryllium, as illustrated in the phase diagram (Figure 1) in a process designed to smooth the surface of mirrors. The kernel of the idea is that by ion implantation of 10 at. % boron into the surface of Be, one could arrive at the eutectic composition of 90 at. % Be-10 at. % B. Then by heating to the eutectic melting temperature (1120 C), the surface alloy could be melted and mirrors of the material could be melt glazed. The idea is to be able to finish a mirror starting with an as-machined surface texture. The assumption is that single-point turning of curved mirrors to an acceptable figure is reasonably economical but that final polishing by mechanical means has cost, quality-control, safety, and regulatory disadvantages. The described concept is illustrative of the main idea.

However, there are variations on the principle, as well as possible serendipitous effects (good and bad) that might be expected. While the proposed final result appeals to principles of equilibrium chemistry, much of the pathway is in the realm of non-equilibrium chemistry. That is because of the ability of ion implantation to produce the metastable starting state, a uniformly mixed B-Be composition which in equilibrium, would be a two-phased alloy. Various effects are possible.

### **Work and Results to Date:**

- **Samples:** Sample procurement, characterization, selection and preparation. Characterization includes profilometry, optical microscopy, mechanical measurements and weight for density, and Rutherford backscattering (RBS) analysis for purity.
- **Ion Implantation:** Ion implantation and post ion implantation characterizations. Work consists of ion implantation of four samples with boron and one with nitrogen ions. Post implantation characterization consisted of optical microscopy, profilometry and RBS.
- **Heating:** Post implantation heating. Heating has been carried by two approaches. The first attempt was to utilize encapsulation in quartz in conjunction with an IR furnace. This approach was done at Oak Ridge National Laboratory, The STTR partner. The idea was to carry out the heating in a stepwise fashion because of the possibility of unpredicted effects. The nitrogen



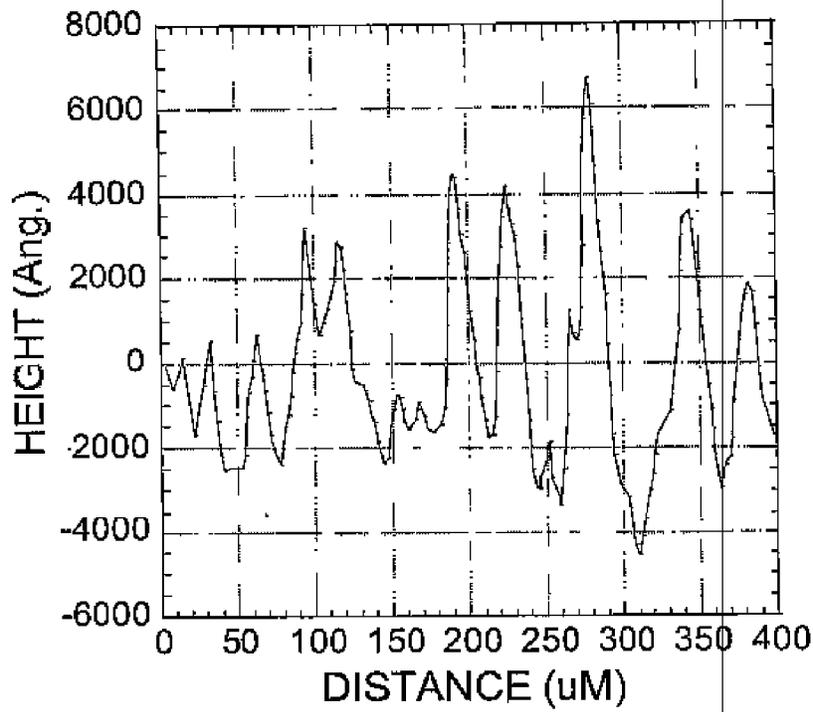


Figure 11: Profilometry trace for the boron implanted sample after heating to 800 C. The  $R_A$  value is 165 nm. This is a portion of a 1 mm trace. Compare with Figure 3 for as-machined material.

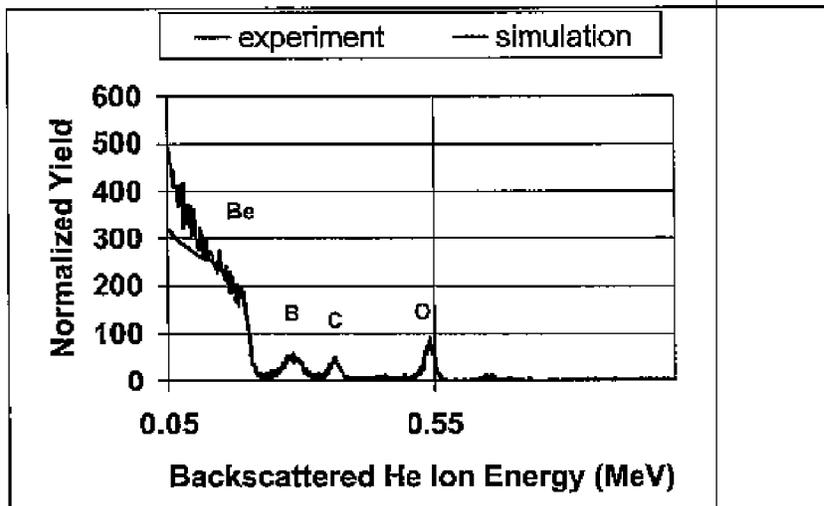


Figure 9: RBS histogram of sample successfully implanted with boron without undue contamination. Three such samples have been produced.

### Heating

The heating procedures proposed and developed at Oak Ridge National Laboratory (ORNL) have been subjected to rigorous examination both by ORNL safety and environmental management and by Brontek also, which has considerable expertise. While fragmentation is not expected, possible evaporation and contamination of equipment is of concern. That issue was a design concern of Brontek anyway from the outset, because of a different issue, that of possible evaporation of the treated surface. This is not expected to happen because there is always some oxide passivation even at the best vacua. The vapor pressure of BeO at 1200C is some  $10^{-32}$  atmospheres. But even if the Be were bare, the short hold times we expect at-temperature are not expected to produce evaporation before melting. Nevertheless, the qualitative issue of safety at ORNL transcends the issue of whether or not the experiment is a success. Therefore a policy of absolute containment has thus far been followed.

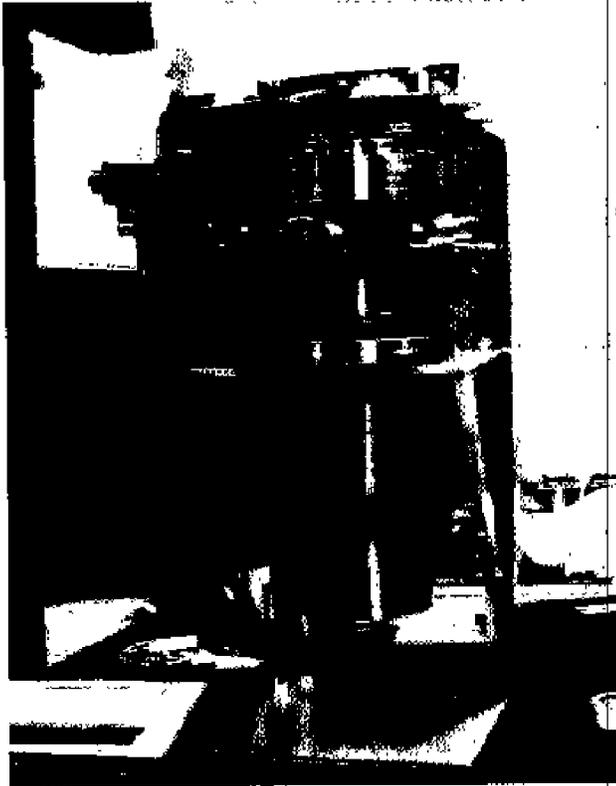


Figure 8: Photograph of the sample manipulator with the dual purpose shroud.



**Figure 6: Photograph of Ion Implantation Chamber and Instrumentation Installed at the Center for Irradiation of Materials, part of Alabama A & M Research Institute at Normal, AL.**

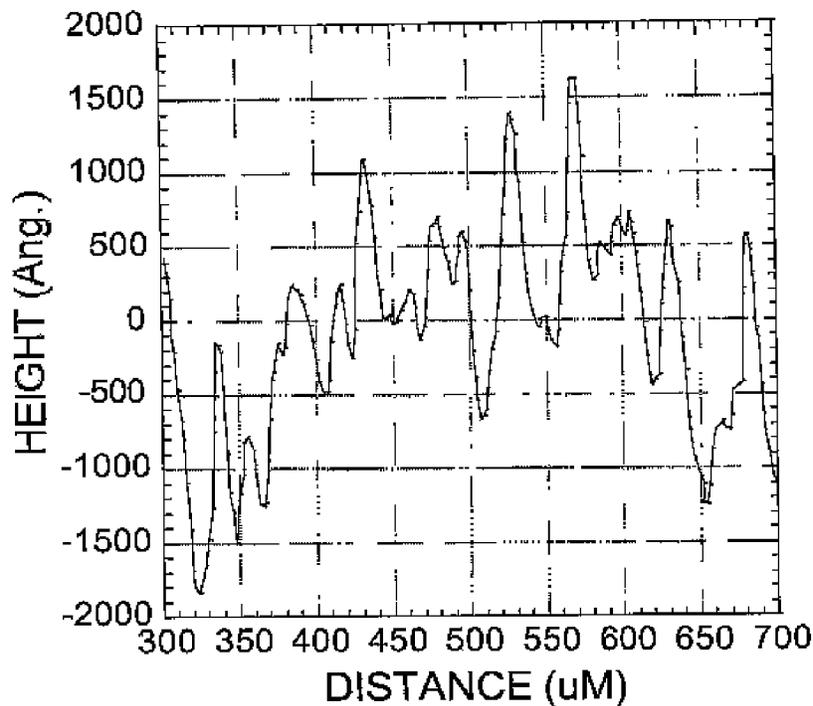


Figure 13: Profilometer trace of the nitrogen implanted sample. The  $R_A$  value is 71 nm. The full trace lengths were 1 mm.

Heating has been done for each capsule at 600, 700 and 800 C thus far by the "ORNL" scheme. The furnace was an infrared radiation furnace. Temperature measurement was by means of a thermocouple spot welded to a dummy sample near the capsule. Ramp times were 3.5 m and soak times were 1 m at each temperature. After each heating, the capsule was cooled and the sample was inspected through the quartz tube. The reason for the stepwise approach is because of the possible unpredictable effects.

There was little difference in the appearance of the two control samples due to the presence of  $O_2$  in one and the absence in the other. However, by 800 C there was some

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filtering of exhaust because of the Be. The system worked well. A photograph is shown in Figure 14.

Four samples were heat treated in the system

1. A virgin control, 1083 C, 1 atm of forming gas
2. Sample 5-2, (the nitrogen implanted sample previously heated to 800 C in a capsule), heated to 1122 C in an atmosphere of 13 mTorr of forming gas.
3. Sample 5-3, ( the boron implanted sample, containing carbon and previously reported on, and also heated to 800 C as described above in a capsule), heated to 1130 C in 13 mTorr of forming gas.
4. Sample 5-4, a "clean" boron implanted sample, not previously heat treated, heated to 1160 C at 13 mTorr.

We had only eight samples, which is more than we planned to produce in the Phase I work plan. Of these, 5 were ion implanted and 3 were used as controls for the heating process.

The disposition of the eight samples was as follows.

<u>Sample #</u>	<u>Implanted/Control</u>	<u>Heated</u>	<u>Atmosphere</u>
5-1	control	800 C	0.1 atm argon/ pyrex
5-2	I (nitrogen/carbon)	1122 C	13 mTorr forming gas
5-3	I (boron/carbon)	1170 C	13 mTorr forming gas
5-4	I (boron)	1160 C	13 mTorr forming gas
4-1	I (boron)	no	
4-2	I (boron)	no	
4-3	control	800 C	vacuum/pyrex
4-4	control	1083 C	1 atm forming gas