STUDY OF STRUCTURAL BEHAVIOR OF THIN FILMS

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SUMMARY

Previous work at Norton Research Corporation showed that composites with high specific properties could be made by adhesively bonding multiple layers of material made by vacuum evaporating either boron or boron carbide onto thin substrates such as aluminum foil, titanium foil, or polyimide film. These composites had properties - tensile strength, compressive strength, tensile modulus - which were isotropic in the plane of the composite. Composite test results gave high values for the specific modulus but the tensile strength data indicated that the strength of the evaporated film was in the range of 60 x 10^3 to 100 x 10^3 psi. This work was directed towards developing methods of increasing the strength of thin boron films. The program was divided into two main parts. The first involved the improvement of methods for the measurement of the strength of thin films. The second was a study of the effect of condensation or deposition temperature on the strength of the films.

Techniques were developed for depositing boron films onto both sides of thin titanium and tantalum foils. Small "dogbone" sections of boron were made by masking. Strain gauges were then mounted on these to measure failure strains when the films were loaded in tension. Test results were consistent with those obtained by flexure tests.

When using titanium foil as a substrate significant interaction between the boron and titanium occurred at 500°C. With tantalum interaction started at about 700°C and was significant at 800°C. With both titanium and tantalum the boron had poor adhesion to the substrate when deposited at temperatures of about 300°C.

Measurements of the failure strains for deposits formed in the range of 300 to 600°C on tantalum substrates indicated that there was a significant increase in strength with deposition temperature. Boron films formed at 380°C had a strength of about 90,000 psi while those formed at 610°C had a strength of 270,000 psi. At the higher temperatures tested (700°C-900°C), boron-tantalum interactions probably degraded the tensile strength.

Scanning electron micrographs of the deposits showed a consistent change in surface morphology with deposition temperature. Deposits formed at 300°C had a very fine structure which closely reproduced the substrate surface morphology. Deposits formed at 600°C and 700°C were coarser in structure. At the higher temperature the deposits resembled the "corn cob" type of surface developed on boron filaments made by chemical vapor deposition.

The most important flaws in the boron films appeared to have been generated by either small globules of boron ejected from the melt or small particles (possibly boron dust) on the substrate prior to deposition.

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INTRODUCTION

The work considered in this report was carried out under Contract No. NASw-2094 for the National Aeronautics and Space Administration. It represents a continuation of the work carried out under earlier NASA programs: namely Contract No. NASw-1802 (1) and Contract No. NASw-1553 (2). The results obtained in these programs - along with other work of Norton Research Corporation - have indicated that composites with high specific properties could be made by adhesively bonding multiple layers of material made by vacuum evaporating either boron or boron carbide onto thin substrates such as aluminum foil, titanium foil, or polyimide film. These composites had the feature that the mechanical properties - tensile strength, compressive strength, tensile modulus - were isotropic in the plane of the composite. This was in contrast to the uniaxial composites of boron filaments and graphite fibers which have high stiffness and strength only in the direction of the fibers. In earlier work, composites with high isotropic modulus were made. However, composite test results indicated that the strengths of the evaporated films were generally in the range of 60×10^3 psi to about 100×10^3 psi. Preliminary analyses of the defects in the evaporated films indicated that imperfections in both the substrate and the deposit were acting as strength limiting factors.

During those studies, progress was hampered by the experimental difficulties associated with the measurement of the tensile strength of thin films. In the course of NASw-1802 program, work was initiated on the direct tensile testing of single strips of foil coated on both sides with boron by vacuum evaporation. While not perfected, the procedure showed sufficient promise to warrant further study.

The main purpose of the program covered in this report has been to investigate the effect of deposition temperature on the strength of vacuum evaporated boron films. The purity of the boron source material used was to be higher than used in earlier work and efforts were directed towards increasing the purity of the deposit by decreasing the background pressure during evaporation. An important part of the program was to further develop the procedures for the measurement of the strength of thin films. In addition, optical and scanning electron microscopy were used to identify strength limiting defects in fracture specimens.

With respect to the work on the scanning electron microscopy, we would like to acknowledge the contributions of Prof. A. S. Argon, Mechanical Engineering Department, M.I.T. for both the actual making of the photomicrographs and their analysis.

EXPERIMENTAL APPROACH AND PROCEDURES

Approach

Earlier work at NRC had shown that the direct tensile testing of thin films was complicated by a number of factors. One of the most important was the effect of the substrate. Since a substrate is necessary to collect the condensing vapor and since the condensation process is not an isothermal room temperature process, stresses are normally developed in the substrate-deposit combination. In the first place, it was desirable to minimize those stresses associated with different thermal expansion coefficients by choosing substrates with coefficients close to that of boron ($6.9 \times 10^{-6}/^{o}C$). Both titanium ($8.5 \times 10^{-6}/^{o}C$) and tantalum ($6.5 \times 10^{-6}/^{o}C$) are suitable in this regard. In addition, it was considered desirable to deposit the boron on relatively thin foils with thicknesses comparable to the desired deposit thickness. There are several reasons for this. Firstly, it is likely that there are substantial temperature transients during the coating process and massive substrates may mask these effects. Secondly, if the volume fraction of the deposit is small, it is difficult to separate the contribution of the deposit from that of the substrate in the analysis of tensile behavior.

A further requirement is that the deposit-substrate combination be relatively flat. In this regard, earlier work (2) had shown that stresses associated with the deposition process could be balanced by depositing alternately on both sides of a substrate foil. In order to keep the substrate normal to the source for the major fraction of the deposition time, the substrates were held normal for about 10 secs. and then rapidly rotated 180° to coat the other side. This process was repeated in a flip-flop mode to build up the desired

deposit thicknesses. In this way, strips of titanium and tantalum foils could be coated on both sides with boron. The strips were flat and in general the coatings were black shiny and free of macroscopic cracks and defects.

Strain gauges could then be mounted on the strips and stress-strain measurements made.

In this program, it was considered desirable to restrict the investigation to boron and to study the effect of substrate temperature on the strength and structure of the deposits. It has been shown (2) that vacuum evaporated boron deposits have many similarities to these made by chemical vapor deposition and consequently it was planned to carry depositions at a series of temperatures from 300°C up to temperatures comparable to that used in the CVD process for boron filament production (1100-1250°C).

Substrate Preparation

Both titanium (0.5 mil) and tantalum (1.0 mil) foils were used. However, early in the program it became obvious that the high reactivity of the boron-titanium system restricted the use of titanium to relatively low temperatures. Consequently, most of the work was done with tantalum as the substrate.

In those instances where the titanium foil was used the following surface treatment was used before vacuum coating. The surfaces were cleaned by consecutively scrubbing in trichlorethylene, acetone, alconox solution and distilled water. The foil was then etched for one minute in nitric acid (18%), hydrofluoric acid (1%), water solution followed by thorough washing with distilled water, methyl ethyl ketone and methanol (ultrasonic) before air drying.

Several methods for surface preparation of tantalum were used in the course of the program. For the major part of the work the tantalum was degreased with trichlorethylene and then etched by immersion in boiling (5 mins.) clorox bleach solution followed by a mixture of nitric acid (1 part conc.) for 3 mins. at room temperature. The chlorox-aqua regia treatment was repeated before thorough washing with water and drying.

In the course of the work, it became apparent that the above chemical polishing procedure did not adequately remove the rolling marks in the tantalum foil. A number of procedures for electropolishing were tried, but none was successful because the high resistivity of the foil resulted in uneven polishing conditions. In addition, embrittlement of the foil often occurred.

A more promising procedure was a combination of mechanical polishing and chemical polishing. A relatively good surface

was produced by polishing the foil with "grey steel cut" followed by buffing with "white rouge." (M.E. Baker, Cambridge, Mass.) When this treatment was followed by chemical polishing with a solution made up of acetic acid (2 parts conc.), sulphuric acid (5 parts conc.) and hydrofluoric acid (1 part 40%) for about 15 mins. at room temperature, a high polish was obtained and rolling marks were eliminated.

Vacuum Coating Procedures

All the vacuum coating was carried out in a bell jar vacuum coater-NRC Model 3177. The boron was evaporated from a water-cooled copper crucible by means of a 180° deflected electron beam. Beam power used during evaporation was 8KW. Typically, the pressure was in the range of 1-5 x 10^{-6} torr.

In order to achieve some degree of temperature control over the substrate during coating, the titanium and tantalum substrates were supported in a "furnace" as shown schematically in Figure 1. The furnace was constructed so as to approximate a black body with the aperture at the bottom being only wide enough to allow complete coating of the samples. The furnace was constructed to give approximately isothermal wall temperatures and the radiational shielding was designed to keep the input power low and heat losses to the main vacuum chamber at a reasonable level.

Previous work had shown that the temperature of the substrate could be monitored by mounting very fine thermocouples on the substrates. However, the mounting of these thermocouples on substrates which were to be rotated was troublesome and time consuming. It was more practical to establish the radiational interchange such that the temperature of the sample was controlled by the furnace walls and not by radiation from the source area heated by the electron beam.

Radiational heat transfer calculations indicated that at the higher temperatures planned for this work the geometry indicated in Figure 1 would control the temperatures of the substrates with ±10°C. Measurements made with a thin stationary thermocouple in the vapor stream confirmed this. At the lower temperatures - less than 600°C - there was a temperature increase on opening the shutter. The increase was 47°C at 500°C and about 62°C at 400°C.

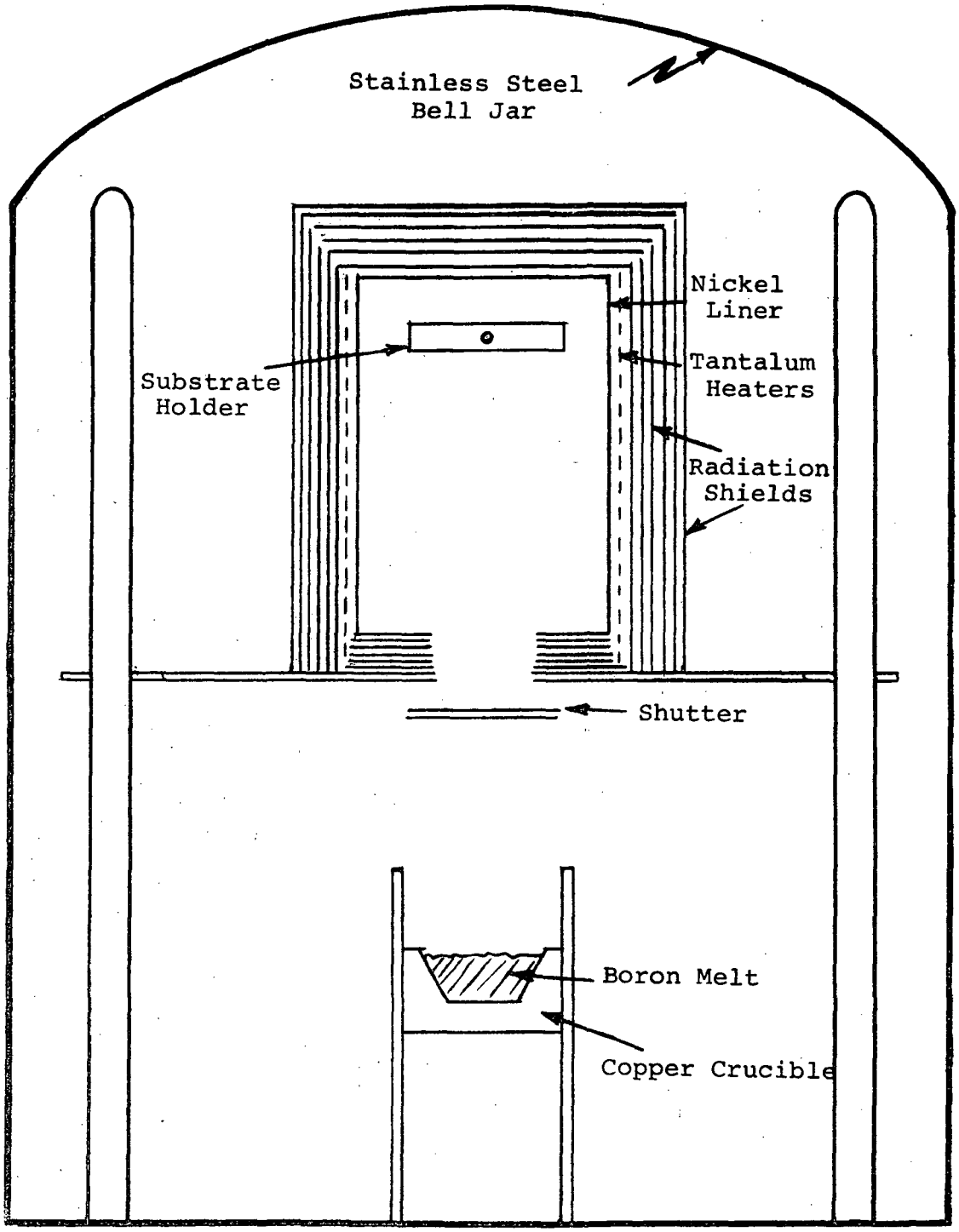

Figure 1. Boron Evaporation Source and Condensation Furnace - Schematic

The substrate holder was mounted within the furnace at a distance 40 cm. above the boron source. In general, three strips of substrate were held in the holder for each run (Fig. 2). During the earlier runs, deposits were made on strips 3/4 in. wide by 4 in. long. In later runs, two strips were coated and a sample of the substrate masked to prevent coating. In this way, stress-strain data could be obtained for both coated and uncoated specimens - each having received similar thermal treatment.

All the specimens were flipped every 10 secs. and the total coating time was 20 min. In this time approximately 0.2 mil of boron was deposited onto each side of the substrate.

The boron used in this program was selected to have a low carbon content. In previous work, so-called high purity boron was found to have low metallic contents but the boron had unspecified amounts of carbon. The boron used in this work contained 0.14% carbon. Emission spectrograph analyses of samples prior to E. B. melting and after melting, gave the results shown in Table I.

A chemical analysis of a sample before melting gave 99.79% boron while a sample from the melt after Run 3177-17 analyzed 98.91% boron.

A residual gas analyzer was used to monitor the gas composition before, during and after the evaporation. While there were a number of minor changes from run to run - mainly dependent on the temperature of the run and the cleanliness of the vacuum system - the major background gases were hydrogen, water vapor, carbon monoxide, and carbon dioxide. In some of the runs there was some evidence of hydrocarbon contamination - presumably from untrapped diffusion pump oil. A typical background gas composition was: hydrogen, 2.2×10^{-6} torr; methane, 1.6×10^{-6} torr; water vapor, 8.4×10^{-7} torr; carbon monoxide, 3.3×10^{-7} torr; carbon dioxide, 2.2×10^{-7} torr.

TABLE I

COMPOSITION OF BORON SOURCE MATERIAL

Element	Before E.B. Melting	After E.B. Melting*
	Concentration Range (%)	Concentration Range (%)
Fe	0.1 - 1.0	0.003 - 0.03
W	0.08 - 0.8	0.10 - 1.0
Co	0.05 - 0.5	0.05 - 0.5
Mn	0.05 - 0.5	< 0.005
Al	0.02 - 0.2	< 0.005
Ni	0.02 - 0.2	< 0.01
Si	0.02 - 0.2	< 0.01
Ca	0.006 - 0.06	< 0.01
Mg	0.003 - 0.03	< 0.005
Cu	0.002 - 0.02	< 0.003
Mo	< 0.005	0.004 - 0.04

*Sample from melt after Run 3177-17.

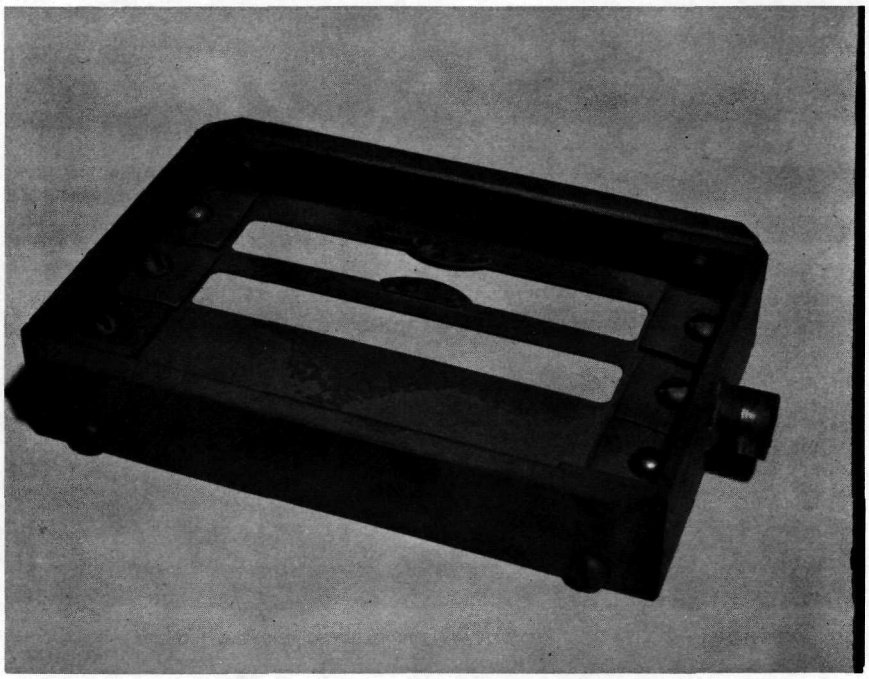

Figure 2. Substrate Holder.

Typical traces of the mass spectra are shown in Figs. 3, 4, and 5 for Runs 3177-8, 3177-13, and 3177-17 respectively. It was significant that there was no clear evidence of the formation of diborane (B_2H_6) or higher boranes. Since the main peak of HBO_2 (Mass 44) is coincident with that of CO_2, it was not possible to distinguish between the two. However, on several occasions there were traces of Mass 43 (HBO_2 with B^{10}) and 62 (H_3BO_3). It is likely that there was a residual concentration of boron-hydrogen-oxygen components but the partial pressures measured during coating were less than 5×10^{-7} torr, assuming the most unlikely case that at the Mass 44 peak represented HBO_2 entirely.

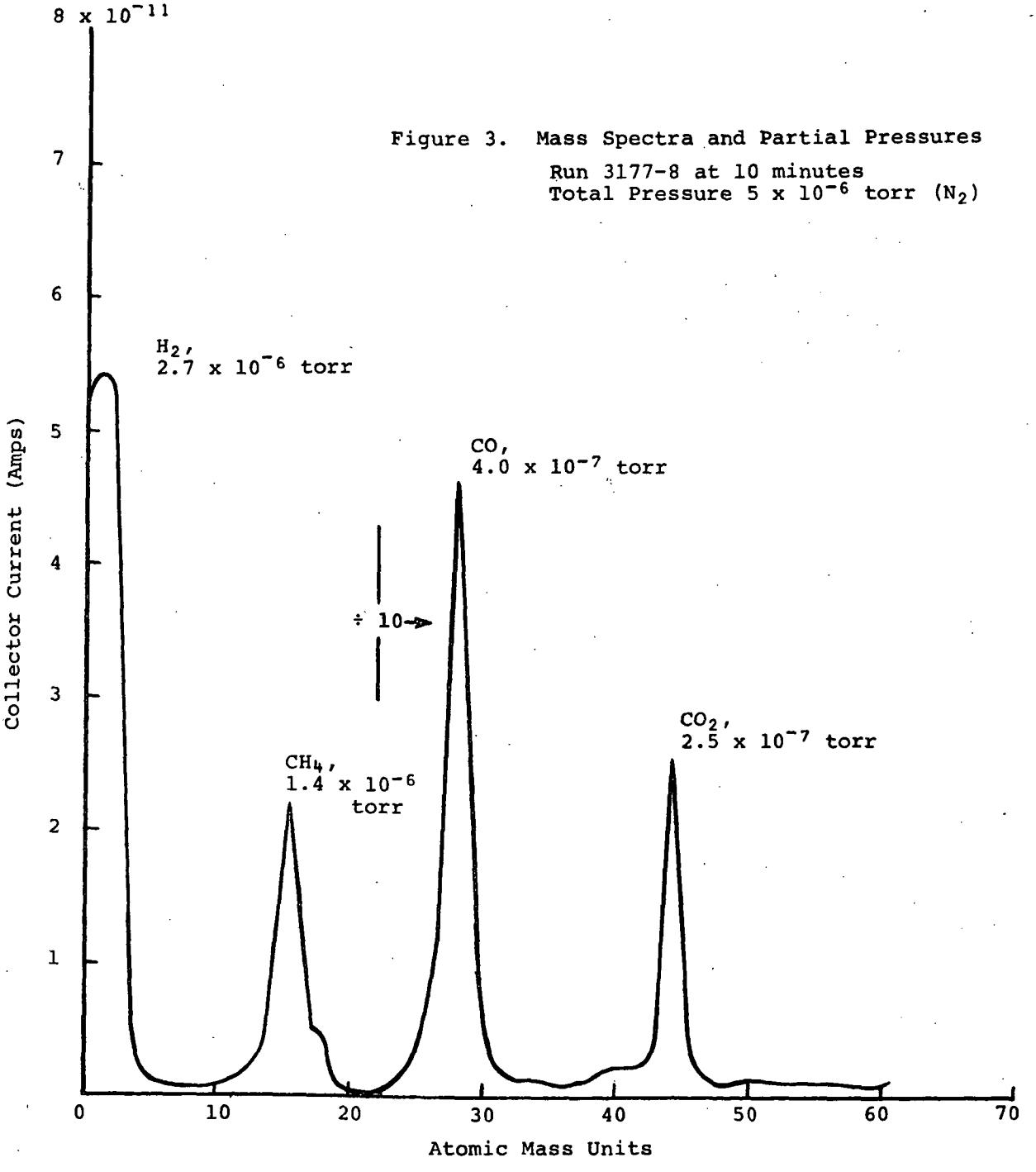

Figure 3. Mass Spectra and Partial Pressures
Run 3177-8 at 10 minutes
Total Pressure 5 x 10^{-6} torr (N_2)

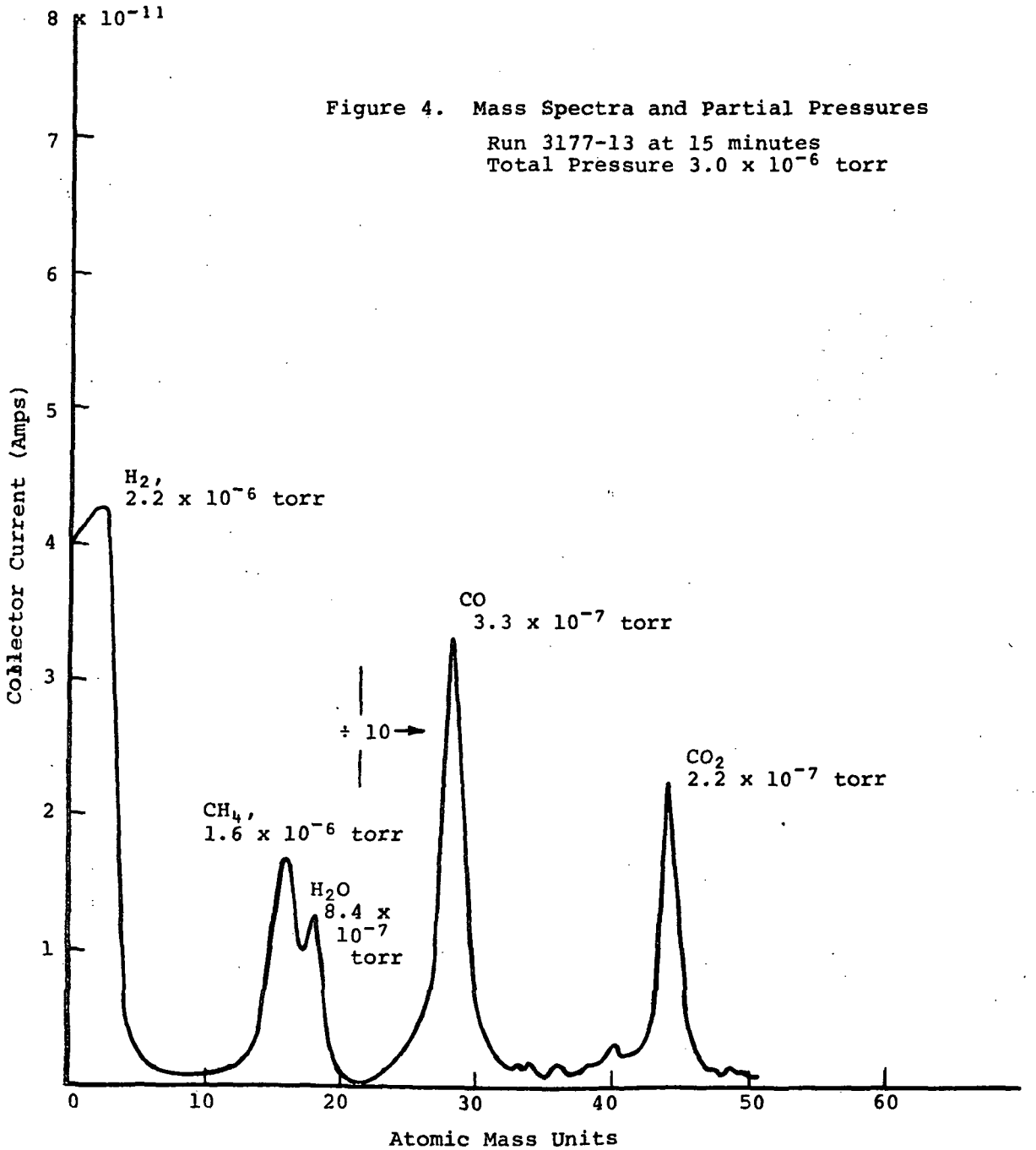

Figure 4. Mass Spectra and Partial Pressures
Run 3177-13 at 15 minutes
Total Pressure 3.0×10^{-6} torr

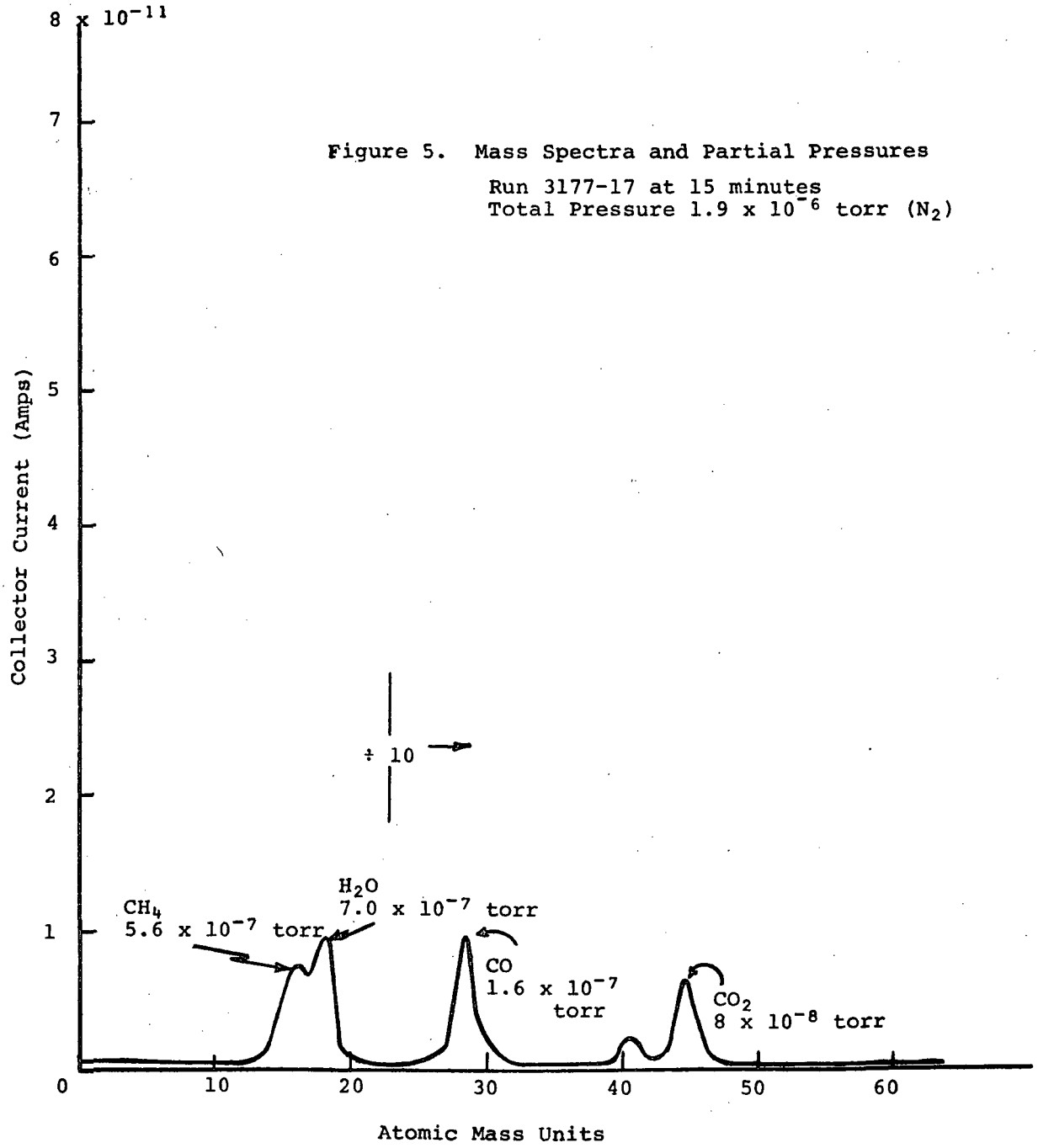

Figure 5. Mass Spectra and Partial Pressures

Run 3177-17 at 15 minutes
Total Pressure 1.9 x 10^{-6} torr (N_2)

Test Procedures

After vacuum coating, the specimens were allowed to cool to room temperature (generally overnight) and the vacuum released slowly with argon. A sample from one of the coated specimens was then removed, boiled in water for two hours and "Scotch tape" applied to the dried boron surface. If boron could not be removed with the tape it was considered that the degree of adhesion between the deposit and substrate was adequate for tensile testing.

In the course of the program, a number of different procedures were examined in order to improve the testing procedure. The basic aim was to measure the strain at fracture of the boron by means of strain gauges adhesively bonded to the boron surfaces. Since the modulus of the boron is approximately 60×10^6 psi, the strength of the boron may be readily estimated from the failure strain.

Early in the program, the substrate was cut into strips 3/4 in. wide and boron was coated on the full width of the strip. It was realized that it was very likely that major imperfections would be introduced at the edges of the strips during the cutting of the substrate. It was then likely that these would initiate crack formation during tensile testing. One possible way to overcome this problem was to use grips which were less than 3/4 in. wide so that the edges of the sample would not be loaded as much as the centre. This is the so-called "Orowan Test". A number of samples were tested in this way. Typically, the grips were 3/8 in. wide and a gauge length of 0.30 in. was used. The size of the strain gauge located in the center of the gauge length was 0.125 in. x 0.125 in.

Examination of the test results showed that this type of test gave a stress-strain curve for uncoated tantalum

which was similar with that obtained using full width grips on a straight-sided specimen. However, when the tantalum was coated with boron, the samples invariably failed in the grip region. Cracks developed at the corners of the grips and not under the strain gauges. A number of different gripping methods were tested. These included wider grips (1/2 in.) with rubber pads and adhesively-bonded tapered aluminum grips. Similar results were obtained - cracks developed near the grips and not under the strain gauges.

It was then decided to mask the tantalum strips so that the substrate (3/4 in. wide) was only coated to a width of 1/2 in. This gave the possibility that edge imperfections in the more ductile tantalum would not initiate cracking in the boron. Tests with wide rubber faced grips (1/2 in. and 1 in.) and adhesively bonded grips continued to result in higher strains in the immediate region of the grips. What was needed was a way to impart higher strains to the boron in the test region. Two approaches were tried. In the first, the tantalum substrate width was reduced in the gauge length to make a "dogbone" type specimen. In the second, the width of the tantalum strip was kept constant, but the size of the mask in the region of the gauge length was increased in area and shaped to make a necked reduction in the area of boron coating (Figure 6). This approach was the more satisfactory. With it, higher strains could generally be developed in the boron and failure strains measured. However, the gripping problem still remained a significant one and there were instances when failure occurred in the grip region and not under the strain gauges. In these cases the maximum strain gauge reading was taken as a lower bound of the failure strain of the boron.

In order to more closely define the actual failure strain of the boron, a number of methods were investigated

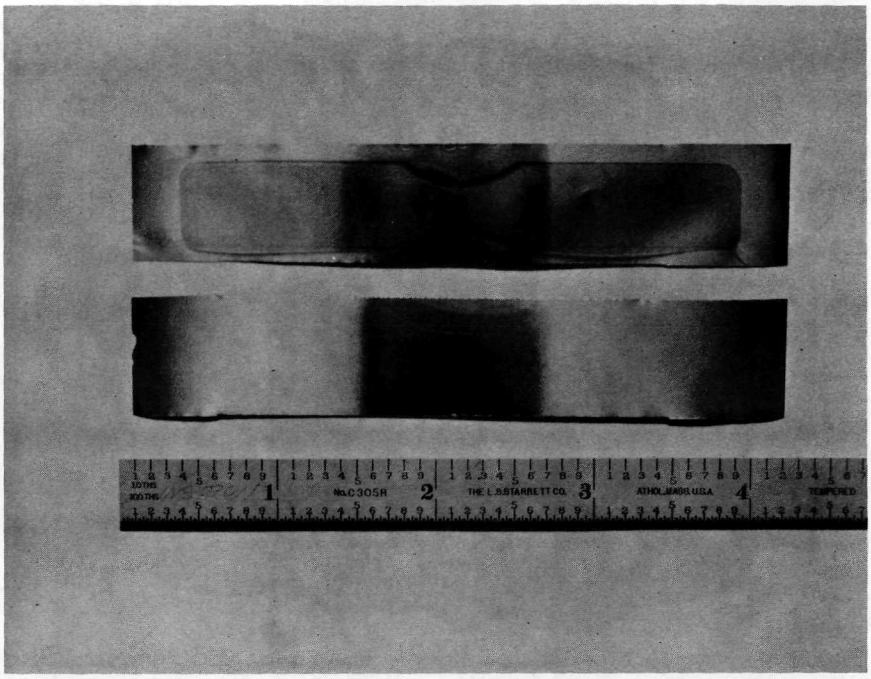

Figure 6. Tantalum Strip With and Without Necked Boron Coating (Dark Central Strip was Buffed Area)

relate crack initiation under the strain gauge to the strain gauge reading. The basic procedure was analysis of the stress-strain curve of the boron-coated substrate and its comparison with the measured stress-strain curve of the uncoated substrate. In many instances, perturbations in the stress-strain curve could be associated with crack development.

In previous work with multilayered laminates, audible cracking had been observed before the specimen failed in tension. Consequently, some effort was directed to amplifying the output of a microphone located near the specimens tested in the current program. The technique was not successful because of the Instron machine noises. The most reliable method was to rely on visual observation. Strains were increased until a few cracks developed in the specimen - often in the region of the grips. The tensile specimen was then removed from the Instron and the strain gauges taken from both sides of the specimen. The sample was then examined carefully under the microscope - sometimes with slight flexure - to ascertain whether or not cracks had developed in the coating.

In the latter part of the program (subsequent to Run 3177-8), the general procedure was to take three samples from a single sheet of tantalum foil for mounting into the vacuum evaporator. One sample was completely masked so as to remain uncoated. A second sample was masked to give the necked tensile specimen for strain gauge measurements. The third sample was masked to give a straight-sided specimen with the coating about 1/2 in. wide. This sample was used to measure coating thickness - calculated from the weight increase during coating. The sample was also used to estimate the tensile strength of the deposit by flexural testing.

From the data obtained in the stress-strain analysis a range of strains of interest was determined. A sample of the boron-coated tantalum could then be pulled around mandrels of decreasing diameter in order to develop increased tensile strains in the outer boron surface. Since the tensile and compressive moduli of boron are equal and since the specimens were coated evenly on both sides of the substrate, it was assumed that the neutral axis in bending the sample was in the center of the tantalum. The outer-surface strain could then be calculated from the radius of curvature and the thicknesses of the substrate and coating.

Boron Morphology and Fractography

Both optical and scanning electromicroscopy were used to examine the morphology of the boron deposits and the nature of crack initiating defects. Since boron is a relatively good electrical insulator at room temperature it was necessary to deposit a thin film of gold on the samples before examination in the scanning electron microscope.

DISCUSSION OF RESULTS

Vacuum Coating and Mechanical Testing

The run conditions maintained in the current program are summarized in Tables II and III. The substrate temperature varied from about 300°C to 900°C. In general, the pressure during deposition was in the low 10^{-6} torr range. The period of coating was 20 minutes for each run, the samples being "flipped" every 10 secs. The measured thicknesses of the deposits were 0.19 ±0.03 mils per side.

In the earlier runs (3177-1 through 3177-5) both titanium (0.5 mil) and tantalum (1.0 mil) foils were used as substrates. However, at a substrate temperature of about 500°C, there was significant interaction between the boron and titanium. When lower temperatures were used to reduce the degree of chemical interaction, the adherence of the boron to the titanium was not satisfactory. Since it was the aim of this program to cover as large a range of substrate temperatures as possible, titanium was not used after Run 3177-5. Work was confined to the tantalum foil. Although the adhesion between the tantalum and boron was unsatisfactory in Run 3177-3 (Sample No. 3) and Run 3177-4 (Sample No. 3) at 300°C and 400°C respectively, samples coated later in the program - namely in Runs 3177-16 and 3177-17 - showed that excellent adhesion could be obtained at temperatures as low as 345°C. The reason for the poor adherence in the earlier runs was not determined.

At the higher temperatures, interaction between the tantalum substrate and the boron occurred at 900°C (Run 3177-6). The coating was dull and powdery. It was porous, could be scraped from the substrate, and appeared partially crystalline under relatively low magnification (50x). The substrates did not remain flat during the coating operation and were warped

TABLE II

SUMMARY OF COATING CONDITIONS

Run No.	Temperature Range °C	Pressure Range (x 10^{-6} torr)	Remarks
3177-1	508-516	9.0-6.8	Ti & Ta Some spitting
3177-2	501-525	1.0-3.0	Ti & Ta
3177-3	300-326	1.0-2.0	Ti & Ta
3177-4	402-407	2.0-5.0	Ti & Ta Beam interrupted
3177-5	697-702	1.6-5.0	Ti & Ta
3177-6	901-906	1.0-7.0	Ta
3177-7	793-807	3.4-5.6	
3177-8	485-522	6.0-4.6	Low carbon boron Ta annealed 1100°
3177-9	697-721	4.0-3.2	
3177-10	508-569	8.0-4.0	
3177-11	395-457	3.0-2.0	
3177-12	602-618	5.0-3.0	
3177-13	694-711	1.0-4.0	
3177-14	795-805	6.0-2.0	
3177-15	516-555	7.0-3.2	Ta annealed 600°
3177-16	443-508	5.6-3.4	Substrate buffed
3177-17	345-426	4.0-1.9	Substrate buffed

when removed from the vacuum system. In Run 3177-7, where the substrate temperature was maintained at 800°C, the degree of each of the above effects was reduced but the samples were still dull, powdery and distortion of the substrate had occurred. Similar results were obtained late in Run 3177-14 at 800°C. At 700°C (Runs 3177-9 and 3177-13) the coatings appeared satisfactory for tensile testing. However, a later, more detailed examination of the surface structure by means of scanning electron microscopy and x-ray diffraction showed that there was some evidence of tantalum-boron interactions in the samples prepared at 700°C. (These data are discussed in more detail later in this report.)

In general, the substrate temperature range available for investigation was then restricted by two bounds. The lower limit (300°C) was the lowest temperature at which satisfactory adhesion between the boron and substrate was obtained. The upper limit (approximately 700°C) was determined by chemical interaction between the boron and tantalum substrate.

Within the range 300-700°C, estimates of the strain at which failure in tension occurred in the boron film deposits were made. The methods used were described earlier in this report under "Testing Procedures". The results have been summarized in Table III and Figure 7.

Because of stress concentrations associated with the grips used in the tensile testing, in many cases failure occurred in the test samples in regions outside the area covered by the strain gauges. In these instances, microscopic examination of the area under the strain gauge (after removal) showed that cracking had not occurred. In these cases, the maximum strain gauge reading was less than the failure strain of the boron film. In a case where stress concentrations did not occur at the grips the strain was increased until one or two cracks

TABLE III

SUMMARY OF TEST RESULTS

Run No.	Sample	Substrate	Failure Strain %	Remarks
3177-1	1	Ti	NT	Ti-B reaction
	2	Ti	NT	Ti-B reaction
	3	Ta	NT	Adhesion test
3177-2	1	Ti	NT	Ti-B reaction
	2	Ti	NT	Ti-B reaction
	3	Ta	0.28	Orowan test
3177-3	1	Ti	NT	Poor adhesion
	2	Ti	NT	Poor adhesion
	3	Ta	NT	Poor adhesion
3177-4	1	Ti	NT	Poor adhesion
	2	Ti	NT	Poor adhesion
	3	Ta	NT	Poor adhesion
3177-5	1	Ti	NT	Ti-B reaction
	2	Ta	>0.16	Orowan test
	3	Ta	>0.14	Orowan test
3177-6	1	Ta	0	Powder deposit
	2	Ta	0	Powder deposit
	3	Ta	0	Powder deposit
3177-7	1	Ta	0	Powder deposit
	2	Ta	0	Powder deposit
	3	Ta	0	Powder deposit
3177-8	1	Ta	>.17	Orowan test
	2	Ta	>.16	Orowan test
	3	Ta	>.19	Orowan test
3177-9	1	Ta	0.32	Ta masked
	2	Ta	>.21	½ in. Al grips
	3	Ta	>.22	Orowan test

TABLE III CONTINUED

Run No.	Sample	Substrate	Failure Strain %	Remarks
3177-10	1	Ta	>.27	Orowan test
	2	Ta	>.28	½ in. Al grips
	3	Ta	.36	Ta uncoated
3177-11	1	Ta	.27	Orowan test
	2	Ta	.28	Ta notched
	3	Ta	.36	Ta uncoated
3177-12	1	Ta	.44	Dogbone
	2	Ta	.46	Bend test
	3	Ta	.32 yield	Ta uncoated
3177-13	1	Ta	>.33	Failed near grip
	2	Ta	.37	Bend test
	3	Ta	.33	Ta uncoated
3177-14	1	Ta	NT	Ta-B reaction
	2	Ta	NT	Ta-B reaction
	3	Ta	0.26	Ta uncoated
3177-15	1	Ta	>0.37	Dogbone
	2	Ta	0.30	Bend test
	3	Ta	0.41	Ta uncoated
3177-16	1	Ta	>0.25	Dogbone
	2	Ta	0.25	Bend test
	3	Ta	0.36	Ta uncoated
3177-17	1	Ta	0.15	Dogbone
	2	Ta	0.17	Bend test
	3	Ta	.33	Ta uncoated

NT = Unsuitable Sample - Not Tested

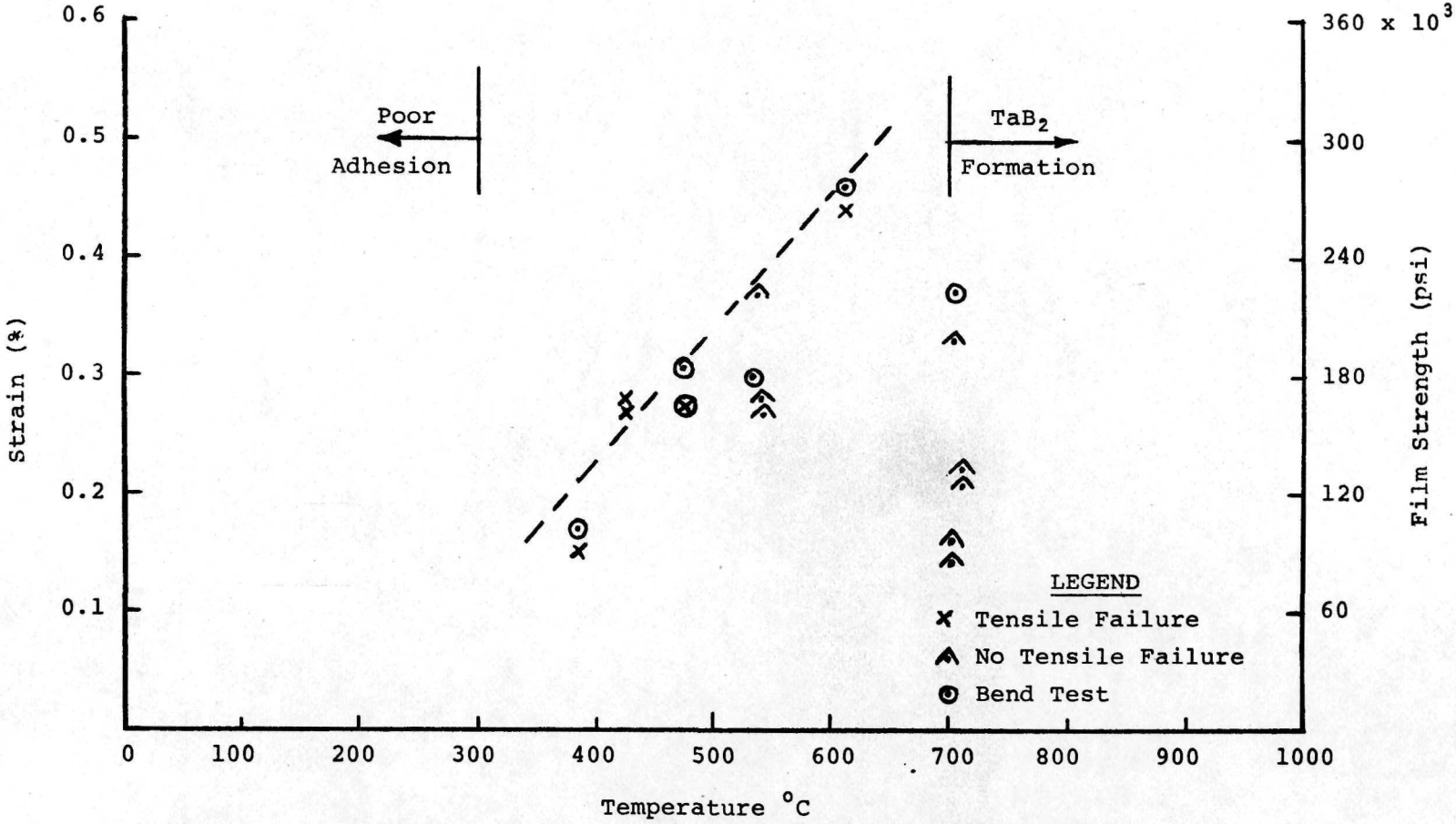

Figure 7. Effect of Substrate Temperature on Failure Strain and Strength of Boron Films

formed under the gauge. This could then be taken to be the failure strain of the boron film.

In all cases, strain gauges were mounted on both sides of specimen tested to cancel out bending components. In addition a stress-strain curve was also obtained for the uncoated tantalum strips in each run. Care was taken to give the uncoated substrate specimens the same surface and temperature treatments as the substrates which were coated.

By comparing the stress-strain curves for the coated and uncoated specimens, the contribution of the boron film to the stress-strain behavior of the coated specimen could be calculated.

For example, Figure 8 is the stress-strain curve obtained for Sample 1 from Run 3177-12. Figure 9 is the stress-strain curve for the uncoated tantalum from the same run. The initial linear section in the Figure 9 (up to a strain of 0.27%) represents elastic behavior in the boron-tantalum combination. The modulus 32.9 x 10^6 psi is close to that calculated by the law of mixture from the known moduli of the tantalum (27 x 10^6 psi) and boron (60 x 10^6 psi) and the respective volume fractions of each component. From the stress-strain curve of the uncoated tantalum it may be seen that the yield strain was 0.30%. The second linear section in Figure 9 (from 0.32% strain to 0.44% strain) resulted from a combination of elastic behavior of the boron and plastic extension of the tantalum. The slope of the linear section of the stress-strain curve in this region corresponds to a modulus in the boron of 59.0 x 10^6 psi. The boron then failed at a strain of 0.44% and the tantalum continued to yield to an average strain gauge reading of about 0.51%.

The above general analysis was supported by data obtained by bend testing. Samples of boron-coated tantalum coated in the same experiment (Run 3177-12) were bent around mandrels

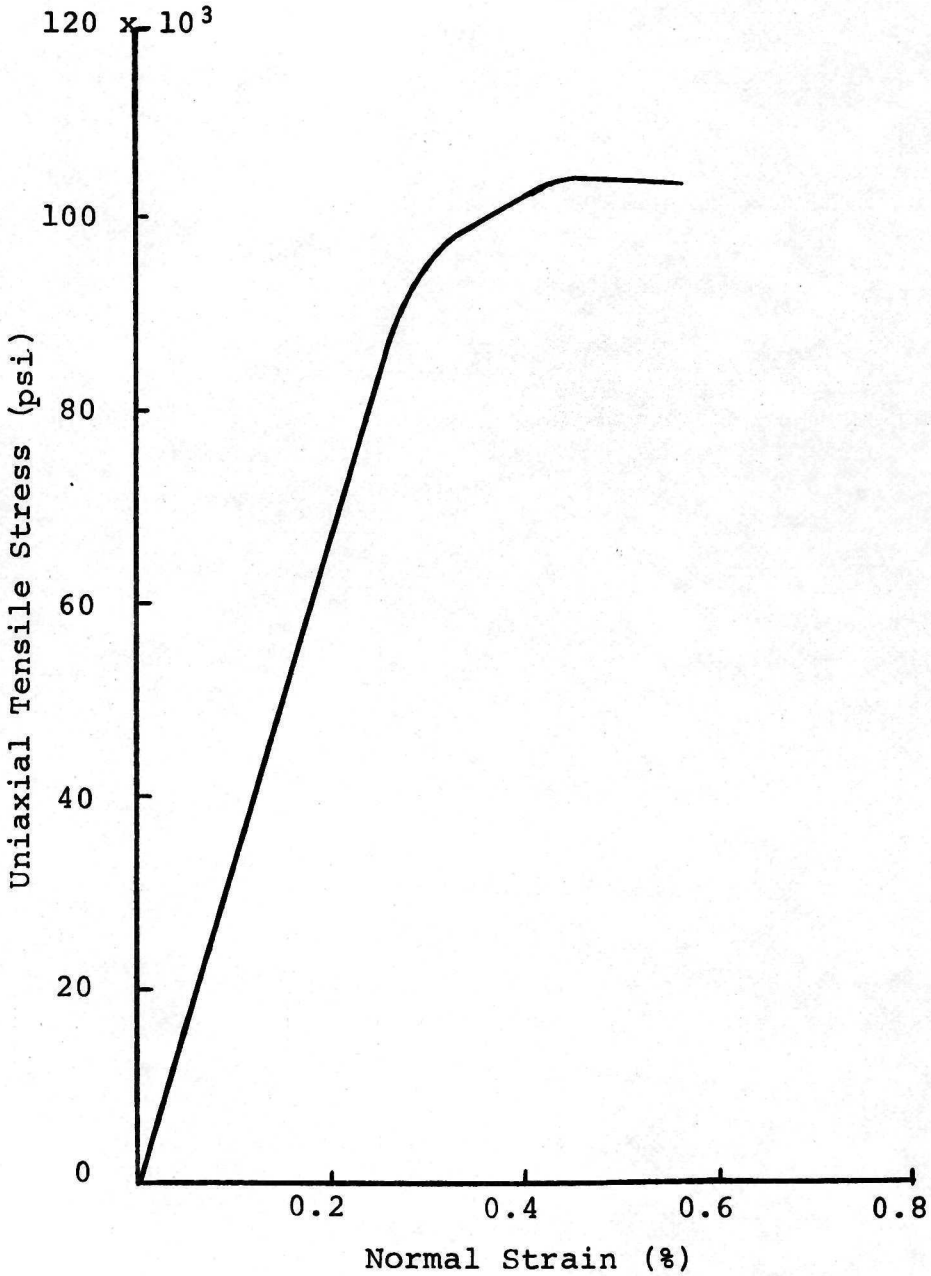

Figure 8. Stress-Strain Curve for Boron Coated Tantalum
Run 3177-12, Sample No. 1 (610°C)

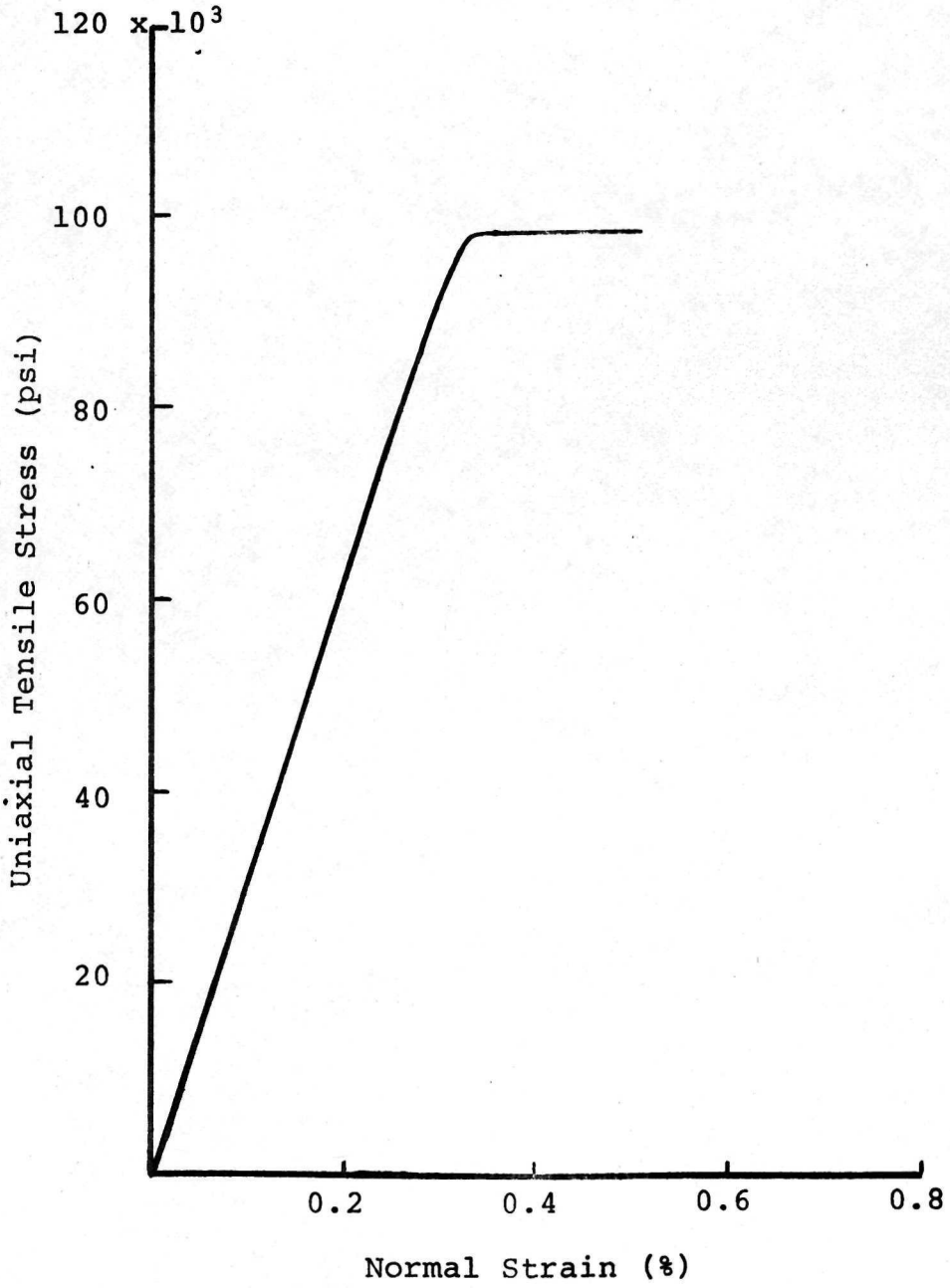

Figure 9. Stress-Strain Curve for Uncoated Tantalum
Run 3177-12, Sample No. 3 (610°C)

of decreasing diameter until cracks developed in the outer boron surface. Since the boron thickness on both sides of the tantalum was the same, it was assumed that the neutral axis in bending was at the center of the tantalum. This also assumed that the modulus of boron in tension equaled that in compression and that the compressive strength was greater than the tensile strength. The failure strain could then be approximated from $\varepsilon = \frac{t}{2R}$, where t was the total thickness of the boron-tantalum composite and R was radius of the smallest mandrel which did not produce cracking in the outer layer of boron.

In those instances where the boron failed while the tantalum was in the elastic range, similar analysis of the stress-strain data gave a quantitative measurement of the failure strain as long as failure occurred under the strain gauges.

The data in Figure 7 suggest that there is a strong positive relationship between the failure strain of the boron film and the temperature of the substrate during deposition. The measured failure strains (.45% approximately) of films deposited at 600°C was approximately three times the failure strains (approximately 0.16%) obtained for films deposited at 385°C. While there are a large number of ways in which the strength of a brittle material such as boron may be reduced, it appears that there was an over-riding influence of the temperature of the substrate in this work. The strength increased continually from 90×10^3 psi at 300°C to approximately 270×10^3 psi at 600°C. Above 600°C, the strength reductions could be attributed to interaction between the tantalum and boron to form tantalum diboride. Consequently, it is possible that higher strengths would be obtainable at temperatures above 600°C if ways were found to suppress the reaction between the boron and substrate.

In the course of the work several other variables which may have had an effect on the strength of the deposit were considered along with the effect of temperature. Probably the most important of these was the surface finish of the tantalum substrate. As outlined in the earlier part of this report a number of cleaning and polishing procedures were investigated in an attempt to reduce the effects of the rolling marks on the surface of the tantalum substrate. The buffing and chemical polishing procedures used in Runs 3177-16 and 3177-17 produced the smoothest surfaces. A comparison of the failure strain of boron deposited on a buffed surface with that deposited on an unbuffed surface indicated that the buffed surface gave a higher failure strain by 0.06%. While it is likely (see later information from scanning electron micrography) that surface defects have an important effect on film strength, it is unlikely that substrate surface imperfections caused the variations in film strength (or failure strain) measured in this work.

A second variable which was altered was the degree of annealing of the tantalum substrate prior to coating. The substrate material used in Run 3177-8 was vacuum annealed at 1100°C and that used in Run 3177-15 was heat treated at 600°C before coating. The procedure used in most of the runs was to heat the substrates to 50°C higher than the coating temperature for 30 mins. before cooling to the temperature chosen to commence coating. Consequently, while each set of substrates in a run received the same treatment (and in general one sample was masked so as to remain uncoated) there was the possibility of a difference in the mechanical properties of the substrate from run to run. Nevertheless, test results indicated that the mechanical properties of the substrate tantalum did not change to a marked degree. It is unlikely that the variations measured for the boron failure

strains could be attributed to small variations in the mechanical properties of the substrate. The main variations appeared to be related to differences in the structure of the deposit as affected by the substrate temperature during deposition. Some of the effects of temperature were revealed during the work with the scanning electron microscope summarized below.

Morphology and Fractography

After measuring the failure strains of the boron deposits, samples were taken for examination with the optical and scanning electron microscopes. In general, far more detailed information was obtained from the scanning microscope. Figures 10 through 20 are typical examples of the type of micrographs obtained. Consider first Figures 10 through 16, which form a series covering substrate temperatures from 426°C to 800°C. In Figure 10, at a magnification of 10,000, the main boron deposit shows very fine structure and a series of defects (probably reproduced from the substrate) which may have initiated the crack which runs vertically through the micrograph.

Figure 11 is a micrograph of the surface of boron deposited onto a tantalum substrate held at 538°C average temperature. In this case, there is a significant amount of surface structure apparent at 10,000 X. In the upper part of the micrograph there is what appears to be a crevice in the deposit. It is possible that this resulted from a scratch or rolling mark in the tantalum substrate which was not completely filled with boron.

Figure 12 shows a crack in a deposit made at 610°C. Figure 13 shows the surface structure for a deposit formed at an average temperature of 703°C. In the series Figure 10 through 13,

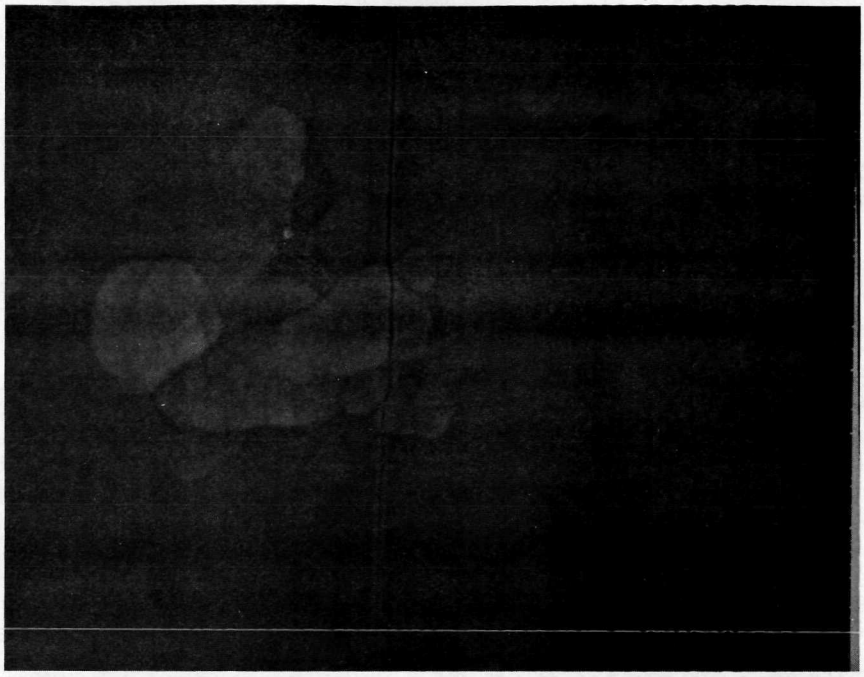

Figure 10. Boron Deposit, Run 3177-11 (426°C), with Defects and Crack (x10,000)

Figure 11. Boron Deposit, Run 3177-10 (538°C), with Defects (x10,000)

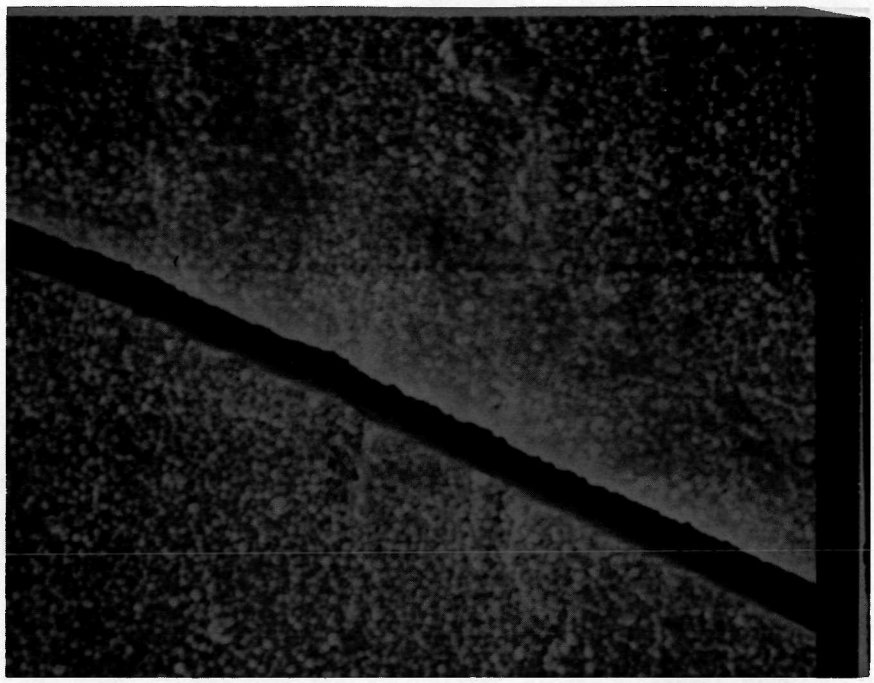

Figure 12. Boron Deposit, Run 3177-12 (610°C), with Crack (x10,000)

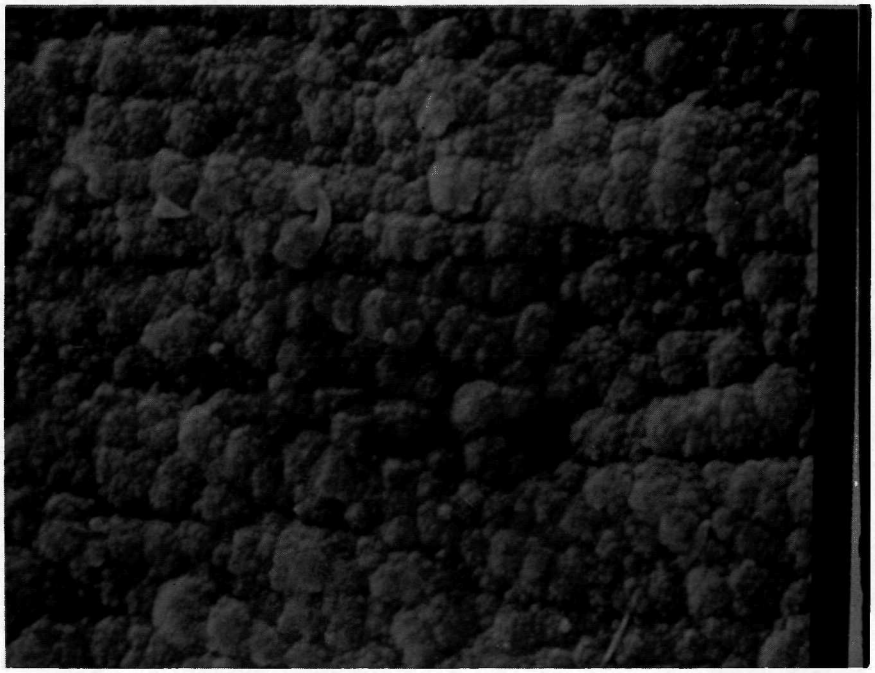

Figure 13. Boron Deposit, Run 3177-13 (703°C), (x10,000)

it is apparent that there was a significant increase in the coarseness of the structure as the temperature of the substrate was increased. The structure shown in Figure 13 is a "cauliflower" type of structure and is reminiscent of the "corn cob" type of surface structure obtained in the C.V.D. formation of boron filaments. The stratification in the surface structure appeared to be related to the rolling marks in the tantalum substrate.

As the temperature was further increased to 800°C (Figure 14), tantalum diboride formation started at specific locations in the deposit. Figures 15 and 16 are micrographs at higher magnifications of the interaction products. Since the interaction products showed some degree of crystallinity (Figure 16), it is not unlikely that each tantalum diboride inclusion formed as the result of reaction of the tantalum substrate with a relatively large globule of boron. The sensible heat of the boron together with the enthalpy of reaction between the boron and tantalum may have been sufficient to maintain the tantalum diboride in a liquid phase prior to crystallization.

The right hand side of Figure 16 shows again the relatively coarse structure of the boron formed at the higher temperatures.

The surface structure shown in Figure 12, suggested the possibility that the deposit was made up of loosely sintered particles of boron. Such a structure would not be fully dense. The porosity would be high and the strength low. Electron micrographs were taken of the edges of cracks to examine the internal structure. Figure 17 is a micrograph of the full cross-section of a boron layer deposited at 600°C. The surface shows very little structure - certainly significantly less than suggested by the surface. Figure 18 is a micrograph showing both the surface of a deposit and the surface

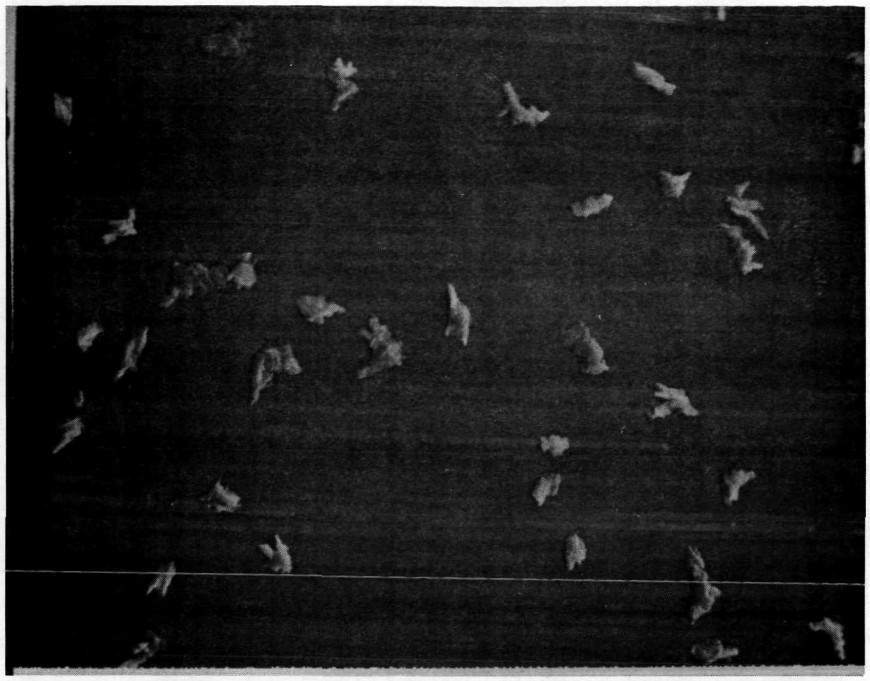

Figure 14. Boron Deposit, Run 3177-14 (800°C) with TaB_2 Formation (x300)

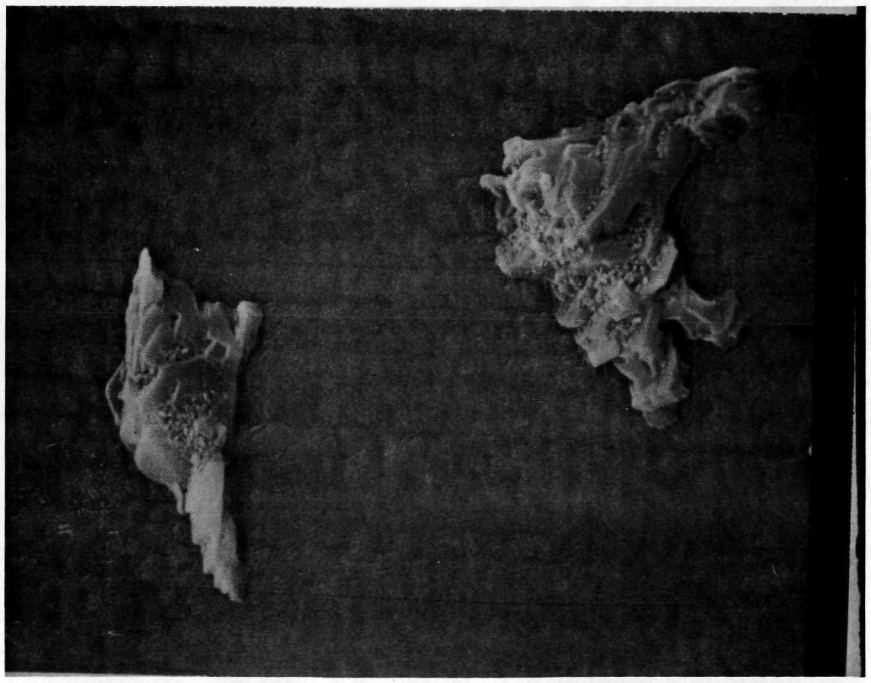

Figure 15. Tantalum Diboride Formation, Run 3177-14 (800°C), (x1650)

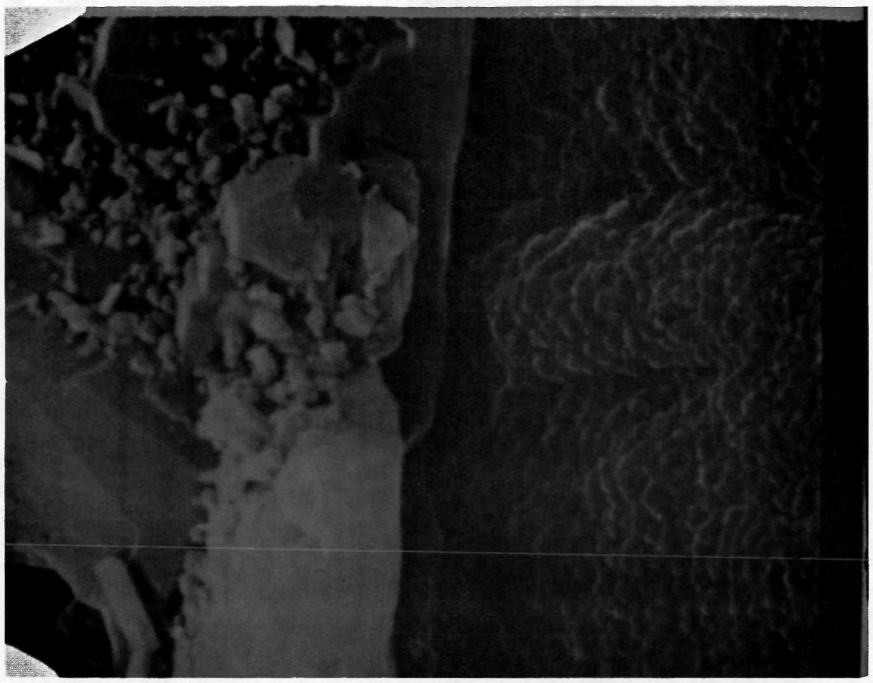

Figure 16. Tantalum Diboride and Boron, Run 3177-14 (800°C), (x10,000)

Figure 17. Internal Structure of Boron, Run 3177-12 (610°C), (x10,000)

of a crack in that deposit. The boron had been formed at 536°C. In this case, there was some internal structure to the deposit. It is possible that the lower strengths obtained for the boron film formed at this run (Run 3177-15 as compared to Run 3177-12) was associated with internal defects and inhomogeneities. These results suggest that it would be advantageious to make accurate measurements of the density of the boron deposits as a function of deposition temperature. It is possible that there is a density increase with deposition temperature which parallels the variation in deposit strength.

In the course of the program, both optical and electron microscopy were also used to detect crack origins. After the development of a tensile crack in a brittle deposit, such as boron, it is generally possible to examine the crack along its length and to locate the crack origin. The origin is usually found at a change in direction of the crack as shown in Figure 19. Defects of this type may be caused by flaws in the substrate, dirt on the substrate and spits and particles forced onto the substrate during deposition. It is significant that in most of the many tensile cracks examined, the limited flaw was similar to that shown in Figure 19. The flaw was commensurate in size to the thickness of the deposit and in most cases appeared to be either dirt or spits of boron (Figure 20).

For the scanning electron micrographs shown in the above figures, the tantalum substrate surface was as shown in Figure 21. It was clear that the tantalum surface did have an influence of the general morphology of the deposit. On the other hand, the scale of the structure even in the coarser deposits formed at the higher temperatures was considerably less than the thickness of the deposit. It would be advantageous to examine the structures formed on highly planar

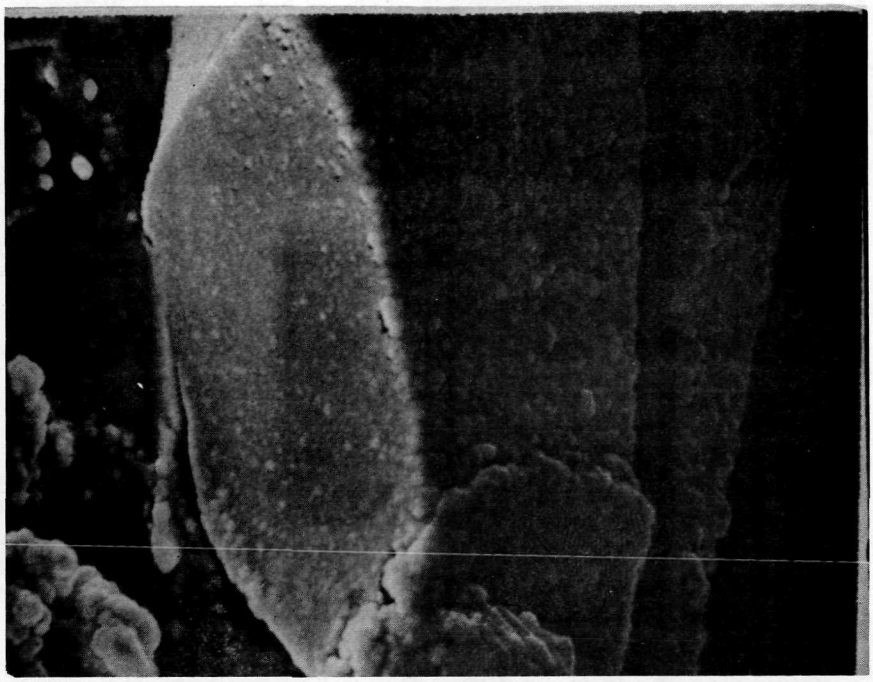

Figure 18. Edge of Crack in Boron, Run 3177-15 (536°C), (x10,000)

Figure 19. Defect and Crack Origin in Boron, Run 3177-12 (610 C), (x5,000)

Figure 20. Crack Origin in Boron, Run 3177-10, (x5000)

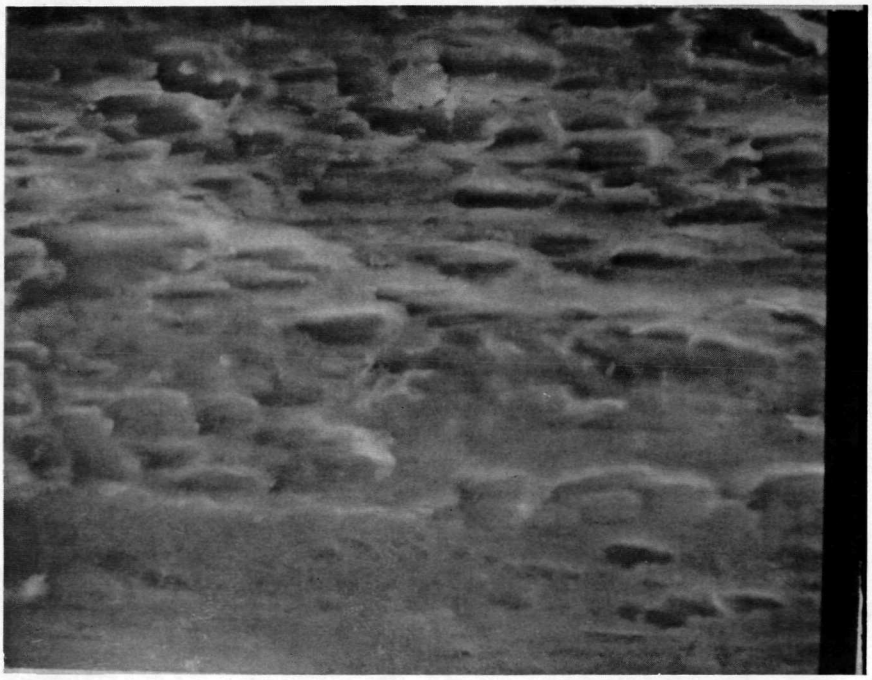

Figure 21. Tantalum Substrate (unbuffed), (x5000)

(polished or cleaved) surfaces as a function of both the temperature of deposition and the thickness of the deposit.

CONCLUSIONS AND RECOMMENDATIONS

Conclusions

1. Vacuum evaporated boron interacted with titanium foil substrate held at temperatures of 500°C and above. Boron began to react with tantalum foil substrate at temperatures of about 700°C. There was significant reaction at 800°C and above to form tantalum diboride.

2. At lower temperatures - in the range of 300-400°C - there was a greater tendency for a low degree of adherence of the boron deposit to both titanium and tantalum.

3. Boron deposited on substrates held at temperatures in the range of 300°C to 800°C showed a consistent change in surface structure. At the lower temperatures, the deposit was fine grained and reproduced the substrate surface finish. At the higher temperatures, the surface structure had a "cauliflower" type of appearance somewhat similar to the "corn cob" type of structure developed on the surface of boron filaments in the C.V.D. process.

4. Scanning electron micrographs (10,000 X) did not reveal any porosity in the deposits made at temperatures as low as 400°C. On the other hand, there was some evidence that the lower temperature deposits had some internal structure.

5. There was relatively good agreement between the failure strain data obtained by strain gauge measurements and those obtained in flexure testing.

6. The strength data derived from the failure strain data indicated that the strength of the boron deposits increased with increases in the temperature of the substrate during deposition. Boron films formed at 380°C had a strength of about 90 x 10^3 psi. Films formed at 610°C had a strength of 270 x 10^3 psi. Since tantalum-boron interactions started

at 700°C, it is likely that the reductions in the strength of the deposits at 700°C and above were related to the formation of tantalum diboride.

7. Surface irregularities in the substrate influenced the surface structure of the boron deposits.

8. Examination of cracks formed in the boron films by tension forces indicated that the most important flaws were inclusions and irregularities which were most likely related to either

a) boron globules ejected from the boron melt;

b) dirt (possibly boron dust) on the substrate prior to depositing the boron.

Recommendations

1. Accurate density measurements should be made of the boron deposits formed at temperatures over the range 300-800°C.

2. Methods for reducing the degree of chemical interaction between the boron film deposit and the substrate should be investigated with the aim of preparing boron films at temperatures in excess of 700°C.

3. The effect of substrate planarity and smoothness on the strength of the boron films should be measured.

4. Methods for reducing the "spitting" from the boron melt should be developed.

5. The effect of the thickness of the boron deposit on the surface structure of the deposit and its strength should be measured.

6. Efforts should be continued to further develop methods for the direct measurement of the strength of thin films.

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