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PROPERTIES OF
VACUUM-EVAPORATED BORON FILMS

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for

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SUMMARY

This report covers work carried out by National Research Corporation on the properties of thin boron films made by vacuum evaporation of elemental boron using an electron beam as the energy source. The work represents a continuation of several earlier programs with the National Aeronautics and Space Administration. The earlier work showed that composites with high specific properties could be made by adhesively bonding multiple layers of material made by evaporating boron onto thin substrates, such as titanium foil or polyimide film. These composites had properties--tensile strength, compressive strength, tensile modulus--which were isotropic in the plane of the composite. Tests on multi-layered composites gave essentially theoretical values for the tensile modulus, but the tensile strength data indicated that the strength of the boron films was highly variable and less than 100 KSI. Tests on films of boron deposited in the previous NASA program indicated that boron strengths of up to 270 KSI could be made. The present program aimed at characterizing the properties of vacuum evaporated films more specifically. The work was directed toward those variables considered to be important in affecting the tensile strength of the boron films. In general, the thickness of the films was less than 0.002 in.

The temperature of the substrate on which the boron was condensed was found to be most important. Three distinctly different forms of boron deposit were produced. Although the transition temperature was not sharply defined, at substrate temperatures of less than approximately 600° C. the boron deposits were amorphous to X-ray. If the substrate were highly polished, the deposits were black and mirror-like. For substrates with coefficients of thermal expansion close to that of boron, the deposits were then continuous and uncracked.

At temperatures in excess of 600° C., two other forms were also produced. With highly polished quartz and sapphire substrates, transparent orange-colored continuous films of boron were formed. The films were highly stressed and changed to curved opaque black flakes when removed from the substrates.

When boron was deposited on rough substrates at temperatures in excess of 600° C., a finely divided powder form of boron was produced. The boron "powder" obviously had no mechanical strength. It was made up of small platelets of boron growing at various angles to one another.

Measurements were also made of the density and X-ray diffraction properties of films produced at different substrate temperatures on a variety of substrates. The density of the boron deposits varied from 2.200 g/cc to 2.357 g/cc. The low density material was produced at 140° C., while the highest density was made at 525° C. The densities of flakes prepared at higher than 525° C. were lower than 2.357 g/cc. However, it is possible that the densities may have changed when the deposits were removed from the substrates. X-ray diffraction studies showed that increased crystallite sizes were produced at higher temperatures. Both tetragonal and rhombohedral phases of boron were found to be present on several substrates. The work indicated that boron films made by vacuum evaporation onto substrates held at 400° C. to 600° C. had similar properties to boron made by chemical vapor deposition at approximately 1200° C.

Studies of the strength of multiple layers of boron and tantalum consecutively deposited on tantalum foil along with tests of boron and titanium consecutively deposited on tantalum indicated that the latter system gave the highest strengths. The highest proportional limit strain measured for the boron was 0.39% equivalent to a strength of 234 KSI. Scanning

electron microscope studies confirmed that the major defects in the deposits were caused by small droplets of boron from the melt impacting the deposit. Several requirements for increasing the strength of boron film composites were developed. The studies suggest that the potential continues to exist for film-type composites to have both high strength and high modulus.

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1. INTRODUCTION

The work considered in this report was carried out under Contract NASW-2214 for the National Aeronautics and Space Administration. It represents a continuation of work carried out under earlier NASA programs; namely, Contract NASW 1802 (1), Contract NASW 1553 (2) and Contract NASW 2094 (3). The results obtained in the above program--along with other work by National Research Corporation and Norton Research Corporation--have shown that composites with moderate specific strength and high specific modulus could be made by adhesively bonding together multiple layers of material made by vacuum evaporating boron onto thin substrates such as aluminum foil, titanium foil, tantalum foil and polyimide film. These composites had the feature that the mechanical properties--tensile strength, compressive strength and tensile modulus--were isotropic in the plane of the laminae. This is in contrast to the uniaxial composites made from boron filaments or graphite fibers. Uniaxial composites made from these materials have high strength and stiffness in the direction of the fibers. The strength and stiffness at right angles to the fibers is determined mainly by the matrix material. For organic matrices such as epoxy and polyimide, both the strength and stiffness are low. Cross-plying of filamentary materials is used to obtain higher mechanical properties in other directions but the inherent strength and stiffness of the boron and graphite are not achieved because the filaments laid down at different angles must be placed in different planes. For instance, if filaments with strengths of 500 KSI are used in a 50 volume percent uniaxial epoxy composite, the resulting strength would be 250 KSI in the fiber direction--but only several thousand KSI at right angles to the fiber direction. If strength is required in all directions in the plane of the composite, the filamentary material must be laid down in 3 or 4 angles to one another to make a pseudo-isotropic composite. The strength would be approximately

75 KSI--and it would be in all directions. Although the inherent strength of filament material may be 500 KSI, the strength of the isotropic composite is about 75 KSI.

Similarly, a filamentary material with a modulus of 60 x 10^6 psi can be made into a uniaxial composite (50 volume percent) with a tensile modulus in the filament direction of 30 x 10^6 psi. The corresponding filamentary pseudo-isotropic composite would have a modulus of about 12 x 10^6 psi.

In contrast, the potential exists for a multi-layered film composite to have high strength and high modulus in all directions. If the same mechanical properties were obtained for boron films as have been obtained for boron filaments, composites (50 volume percent) with strengths of 250 KSI and moduli of 30 x 10^6 psi would be possible.

Boron film composites with high moduli have been made. Tensile and compressive moduli in the range of 20 - 25 x 10^6 psi have been obtained routinely with composites having polymeric matrices and boron contents not exceeding 50%. On the other hand, the highest tensile strength obtained with a boron film composite using polymeric matrices has been 56 KSI (4). Typically the composite strength has been about 40 KSI. It has been apparent that strength of the boron films was variable and considerably lower than theoretically possible.

In the earlier NASA programs, investigations to define the most important variables affecting the strength of vacuum evaporated boron films were initiated. Work also concentrated on the difficult problem of the measurement of the strength of thin films. During the NASW 2094 program, improved measurement techniques were developed (3). The technique involved the deposition of boron on both sides of thin titanium and tantalum foils.

Small "dogbone" sections of boron were vacuum deposited onto these foils through a mask. Strain gauges were then mounted on these to measure failure strains when the films were loaded in tension. Estimates of the tensile strength were then calculated from the proportional limit strain and the known modulus of the boron. The results were consistent with those obtained by flexure tests. Although a significant improvement, the dogbone technique, as developed in NASW 2094, often resulted in tensile failure outside the test area. Further work was required, and it was planned that this would be included in the present program.

Work in NASW 2094 (3) also indicated that the temperature at which the substrate was held during the vacuum coating had a significant effect on strength. 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. (The latter strength was considerably greater than any value computed from results obtained from measurements of the tensile strength of multi-layered composites.) At higher temperatures chemical interaction between the boron and tantalum substrates was considered to be responsible for reductions in the strength of the boron deposits.

Scanning electron micrographs of the boron deposits indicated that the deposits formed at 600-700° C. were coarser in structure than those formed at lower temperatures. At 700° C. the structure resembled the "corn cob" type of surface developed on boron filaments made by chemical vapor deposition.

The most important flaws in the deposits appeared to have been caused by small droplets of boron which, after being ejected from the melt, impacted the boron deposit. The physical damage caused by these droplets was extensive. It was considered likely that the resulting flaws were important limitations to the strength of the films.

With the above information as a basis, the main aims of the present program were as follows:

1.1 To further characterize boron films made by vacuum evaporation and to ascertain in more detail the effects of substrate composition on the physical and mechanical properties of the films.

1.2 To further investigate the effect of substrate temperature on the properties of boron films.

1.3 To obtain X-ray diffraction analyses of boron films and to compare the absorption properties with those of boron made by chemical vapor deposition.

1.4 To measure the density of films made at various temperatures.

1.5 To improve the techniques for the measurement of the strength of thin boron films and to measure the strength of films made under selected conditions.

1.6 To measure the effect of boron film thickness on the strength of the films.

1.7 To further characterize the morphology of boron films using optical and scanning electron-microscopy and to further characterize strength limiting defects.

The experimental work of this program was divided into five main sections. In general, the work involved the preparation of boron film deposits under various sets of controlled conditions. This was followed by the analysis of the physical properties of the deposits by appropriate methods. During the earlier part of the program, the work aimed at finding substrates suitable for boron deposition over relatively wide temperature ranges. A later part of the work involved separation of the boron from the substrate for density measurement and X-ray analyses. In addition, strength measurements were made of boron films which had been deposited on suitable substrates to study the effect of deposit thickness on film strength. These areas of work are considered under the following subject headings:

Effects of Substrate Composition and Temperature
X-Ray Analyses
Density Measurements
Strength of Deposits
Morphology of Deposits

2. EFFECTS OF SUBSTRATE COMPOSITION AND TEMPERATURE

Earlier work at NRC (1) (2) (3) had shown that boron could be deposited on thin substrates such as titanium foil, tantalum foil, molybdenum, tungsten and polyimide films. The NASA program (3) (NASW 2094) preceding the current program, had shown that the strength of boron films deposited on tantalum foil increased with the temperature of deposition. Films formed at 300° C. had a strength of about 90,000 psi, while at 600° C. the strength was about 270,000 psi. The work suggested that higher strengths would be possible if the deposition temperature were increased above 600° C. However, deposition at higher temperatures during that program produced granular deposits of negligible strength. There was evidence of significant chemical interaction between the boron and tantalum.

In order to prepare and study the physical and mechanical properties of thin boron films, a satisfactory substrate was required. Ideally, the substrate should meet the following requirements:

Not interact chemically with boron over the temperature range of interest during deposition.

Have a coefficient of thermal expansion equal to that of boron. If the coefficient of expansions are equal, thermal strains are less likely to be developed between the boron and substrate as a result of temperature changes during and following deposition.

The vacuum deposited boron should adhere to the substrate.

The substrate should be planar with surfaces amenable to high degrees of polishing.

The substrate should be available as a thin sheet or foil comparable in thickness to the boron films under study--preferably less than 1 mil. in thickness.

In addition, experience has shown that it is advantageous for the substrate to be strong, have a relatively low modulus of elasticity, and not be brittle.

These limitations considerably restrict the choice of substrate material. A general survey narrowed the choice to the following: copper, tantalum, alumina, sapphire, boron carbide, quartz and polyimide film. The coefficients of expansion for these materials, together with boron, are presented in Table I. A large number of other candidate materials were eliminated for various reasons; e.g. tungsten foil is too brittle, molybdenum foil develops surface pits.

In all, some 25 vacuum coating experiments were made using the above substrates. The temperature range studied was from room temperature to about 800° C. The apparatus used was essentially the same as that described in the summary report of Contract No. NASW 2094 (3). The vacuum system was an NRC Model 3177 on which was mounted a 24 in. diameter, water-cooled stainless steel bell jar. The boron was evaporated from a water-cooled copper crucible by means of a 180° magnetically deflected electron beam. The beam power used for evaporation was 8 KW. The substrate samples were mounted 15 in. above the evaporation source and were heated radiantly from a well insulated furnace cavity. The coating times were either 10 or 20 minutes, depending on the information required. The pressure during coating was less than 1×10^{-5} torr.

The main coating conditions are summarized in Table II.

TABLE I

COEFFICIENTS OF THERMAL EXPANSION OF BORON AND VARIOUS SUBSTRATE MATERIALS

		Expansion Coefficient (/°C.)
	Boron	6.9×10^{-6}
Metals	Copper	17.8×10^{-6}
	Tantalum	6.5×10^{-6}
	Titanium	8.5×10^{-6}
Refractory Compounds	Alumina	6.8×10^{-6}
	Sapphire	8.0×10^{-6}
	Boron Carbide	3.0×10^{-6}
	Quartz	0.5×10^{-6}
Organic	Polyimide (PI)	4.0×10^{-5}

TABLE II

SUMMARY OF EXPERIMENTAL CONDITIONS

Run No.	Temperature ° C.	Substrate	Comments
3177-18	400	Ta (1.0 mil)	Cu evaporation
3177-19	800	Cu on Ta	Al addition
3177-20	400	Ta (1.0 mil)	Cu evaporation
3177-21	804-817	Cu on Ta	B - 2 sides
3177-22	749-773	Cu (0.5 mil)	B - 2 sides
3177-23	702	Cu (0.5 mil)	1 side - B dull
3177-23	702	Ta (1.0 mil)	1 side - B shiny
3177-24	793-694	Cu (0.5 mil)	2 sides
3177-24	793-694	Ta (1.0 mil)	2 sides
3177-25	525	Cu (0.5 mil)	B shiny-fair adhesion
3177-26	704-713	B_4C (2)	B partial powder
3177-26	704-713	Ta (2) (1 mil)	B partial powder
3177-26	704-713	Cu (2) (35 mil)	B dull adherent
3177-26	704-713	SiO_2 (2)	B mirror-like
3177-26	704-713	Al_2O_3 (1)	B black crystals
3177-27	744-749	SiO_2 (polished)	
3177-27	744-749	SiO_2 (rough)	
3177-27	744-749	SiO_2 (scratched)	
3177-27	744-749	Cu (HNO_3)	
3177-27	744-749	Cu (Etch)	
3177-27	744-749	Cu (polished)	
3177-27	744-749	Al_2O_3	
3177-27	744-749	Cu	
3177-28	508-555	Cu (32 mil)	Plain & scribed

TABLE II - Summary of Experimental Conditions (cont.)

Run No.	Temperature °C.	Substrate	Comments
3177-29	508-534	Cu (32 mil) + BN	
3177-29	508-534	Ta (10 mil) + BN	
3177-30	400-433	Cu (32 mil) + BN	B flaked
3177-30	400-433	Ta (10 mil) + BN	B adherent
3177-31	280-367	PI (0.5 mil)	B shiny adherent
3177-31	280-367	Ta (1 mil) + BN	B flaked
3177-31	280-367	Cu (1 mil) + BN	B - large flakes
3177-32	613-626	Cu (1 mil) + BN	
3177-32	613-626	Ta (1 mil) + BN	
3177-32	613-626	Al_2O_3	
3177-32	613-626	SiO_2 (polished)	
3177-32	613-626	SiO_2 (rough)	
3177-32	613-626	Cu	
3177-32	613-626	Ta	
3177-32	613-626	Sapphire	
3177-33	105-258	PI (0.5 mil)	B flaked
3177-33	105-258	Cu	B flaked
3177-33	105-258	Ta	50% flaked
3177-34	626-642	Sapphire	
3177-34	626-642	SiO_2 + BN	
3177-34	626-642	BN	
3177-34	626-642	SiO_2 (polished)	
3177-34	626-642	SiO_2 (rough)	
3177-34	626-642	Cu	
3177-34	626-642	Ta	
3177-35	602-621	SiO_2 (rough)	
3177-35	(10 min.)	SiO_2 (polished)	

TABLE II - Summary of Experimental Conditions (cont.)

Run No.	Temperature °C.	Substrate	Comments
3177-35*	602-621	Sapphire	
3177-35*	602-621	SiO_2 (polished)	
3177-35*	602-621	Ta (polished)	
3177-36*	400-450	SiO_2 (rough)	
3177-36*	400-450	SiO_2 (polished)	
3177-36*	400-450	Sapphire	
3177-36*	400-450	SiO_2 (polished)	
3177-36*	400-450	Ta (polished)	
3177-37*	508-539	SiO_2 (rough)	
3177-37*	508-539	SiO_2 (polished)	
3177-37*	508-539	Sapphire	
3177-37*	508-539	SiO_2 (polished)	
3177-37*	508-539	Ta (polished)	
3177-38*	307-374	SiO_2 (rough)	
3177-38*	307-374	SiO_2 (polished)	
3177-38*	307-374	Sapphire	
3177-38*	307-374	SiO_2 (polished)	
3177-38*	307-374	Ta (polished)	
3177-39	76-164	PI (0.5 mil)	
3177-39	76-164	Cu (1 mil)	
3177-39	76-164	Ta (1 mil)	
3177-40	25-147	PI (0.5 mil)	
3177-40	25-147	Cu (1 mil) + BN	
3177-40	25-147	Ta (1 mil) + BN	
3177-41	246-295	PI (0.5 mil)	

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* 10 minutes, instead of 20 minutes, coating time was used for these runs

TABLE II - Summary of Experimental Conditions (cont.)

Run No.	Temperature °C.	Substrate	Comments
3177-41	246-295	Cu (1 mil)	
3177-41	246-295	Ta (1 mil)	
3177-42	367-414	PI (0.5 mil)	
3177-42	367-414	Cu (1 mil) + BN	
3177-42	367-414	Ta (1 mil) + BN	

A detailed discussion of each of the runs summarized in Table II is not warranted. It is probably more meaningful to summarize the results on the basis of the various substrate materials investigated. However, before doing so, several general comments should be made. First, it was the aim of a large number of the runs to produce samples of vacuum evaporated boron at known substrate temperatures for later density measurements, X-ray analysis and morphology studies. Consequently, it was desirable to be able to separate the boron from the substrate. In some cases it was possible to dissolve the substrate away from the boron. In other cases it was preferable to have the boron not adhere to the substrate. In a number of instances a thin layer of boron nitride was used as a release agent. In addition, substrates of increased thicknesses were used to increase the thermally induced strains to decrease adherence. If, for instance, boron flakes were required, it was sometimes advantageous to use a thick copper plate as the substrate. Significant thermal stresses would then be set up because of the large difference in thermal expansion coefficients between the boron and copper. With a thick substrate plate the stresses would generally be sufficient to exceed the shear strength at the bond and the boron would flake off.

In the following discussion the main results for each of the substrates studied are summarized.

2.1 Tantalum

Tantalum has a number of obvious advantages as a substrate for boron deposition. It has a coefficient of expansion ($6.5 \times 10^{-6}/^{o}C$) which is close to that of boron ($6.9 \times 10^{-6}/^{o}C$) and tantalum is available in thin gauges (1 mil foil was used extensively in this program). Tantalum has good high temperature properties, is readily annealed in a vacuum and is not brittle. The main drawbacks to the use of tantalum are first, it is reactive to oxygen and oxygen containing gases, and second, it is only dissolved by chemicals which also attack boron. Consequently, it is difficult to etch tantalum substrates away from boron deposits.

In the experimental program, boron was deposited on tantalum at temperatures ranging from room temperature up to 793° C. At the lower temperatures, the adherence of the boron to the tantalum was low. The adherence increased progressively until at about 400° C. it was difficult to remove the boron from the tantalum. At these temperatures, boron nitride release agents coatings were required. As the substrate temperature was further increased to the range of 650 - 700° C., the nature of the coating changed from a black, shiny, continuous film to a dull, gray-brown powder. In the earlier work (3), there was X-ray evidence that the boron had interacted with the tantalum to form tantalum diboride. While some boride formation was also evident in the current work as will be described later, similar boron deposits were also formed on both boron carbide and copper substrates at the same temperatures. It is then more likely that the powdery deposit consisted mainly of boron, but in a significantly different form than produced at lower temperatures. Further details of the transformation are considered later in this report.

Consideration was also given to the possibility that the powder forms of boron produced at the higher temperature might have resulted from reaction between the deposits and the residual gas in the vacuum system during the extensive periods (several hours) of cooling after deposition. In Run 3177-26 (704 - 713° C.), half the samples coated were cooled rapidly after coating while the other half were cooled slowly. Both sets of samples were identical. Powder formation was, therefore, not a result of reaction with residual gases after coating.

It is probable that some boride formation occurs during the initial periods of boron deposition on tantalum. In fact, it is difficult to imagine how the high degrees of boron-tantalum adherence could be achieved without some chemical interaction. But tantalum diboride is isomorphous with boron and it is not unlikely that the boride could nucleate crystallization of the boron.

An additional aspect of interest was that examination of the flakes released from tantalum showed a significant difference in flatness as the temperature of deposition was changed. At low temperature $\sim 300^{\circ}$ C., the flakes were large and flat. As the temperature increased, the flakes first became convex to the substrate, then changed to being flat again at 400 - 450° C. At still higher temperatures (500 - 550° C.), the flakes were concave to the substrate. As the substrate temperature was further increased, the samples became progressively more concave up to the temperature where "powder" formation occurred.

2.2 Copper

The main reason for using copper as a substrate for boron deposition was its low reactivity. Literature studies indicated that copper is one of the few metals which does not readily form borides. This is despite the fact that Hansen (5) reports the existence of a compound for which chemical analyses suggest the formula CuB_{22}. In addition, the solubility of boron in copper is low--approximately 0.09% at 1060° C. On the other hand, the coefficient of thermal expansion is high ($17.8 \times 10^{-6}/^{\circ}C$) compared to boron ($6.9 \times 10^{-6}/^{\circ}C$). Nevertheless, the work with the copper substrate confirmed that a transformation to the discontinuous powder form of boron took place on a copper surface as well as the tantalum at 704 - 744° C. Also, similar flake curvature results to those obtained with tantalum substrates were found for the copper. In general, the flakes were convex to the substrate at 300 - 350° C., flat at 400° C. and became progressively more concave above 500° C. These results indicated that the curvature of the released flakes was not directly related to the coefficient of expansion of the substrate.

2.3 Alumina and Sapphire

Two forms of alumina were used as substrates for boron deposition. High purity alumina (99.5% Al_2O_3) and sapphire. The alumina was in the form of a rod--approximately 1/8 in. diameter with a surface roughness of approximately 20μin. The sapphire was in the form of transparent discs--1/2 in. diameter, 0.020 in thickness with optically polished surfaces. The coefficient of thermal expansion of the alumina was $6.8 \times 10^{-6}/^{\circ}$C. while for sapphire it was $8.0 \times 10^{-6}/^{\circ}$C. Both materials have coefficients of expansion which are close to that of boron--$6.9 \times 10^{-6}/^{\circ}$C.

Boron was deposited on the rough alumina rod at the following temperatures: 613 - 646° C. (Run 3177-32), 704 - 713° C. (Run 3177-26), and 744 - 749° C. (Run 3177-27).

At 613 - 626° C., the <u>initial</u> boron deposit reproduced the surface finish of the alumina. This coating was adherent and there was no evidence of interaction with the substrate. However, it was overcoated with a brown-black powder. At 704 - 713° C., the deposit no longer reproduced the surface. The boron surface was powdery. It was made up of a large number of planar faces with a crystalline appearance. The surface structure was accentuated in that the boron deposit tended to grow as needles from the high points of the substrate surface.

The deposit suggested that there had been significant boron mobility in the deposit formed at 700° C. The deposit formed at 744 - 749° C. was similar to that formed at 704° C. The morphology of these deposits will be considered in more detail in Section 6 of this report.

The above results prompted the testing of the synthetic sapphire as an experimental substrate. Polished sapphire discs were coated at the following temperatures: 307 - 374° C. (Run 3177-38), 400 - 450° C. (Run 3177-36), 508 - 539° C. (Run 3177-37), 602 - 621° C. (Run 3177-35), 613 - 626° C. (Run 3177-32) and 626 - 642° C. (Run 3177-34). In those runs with starting temperatures of 307° C., 400° C. and 508° C., the boron deposits were black, shiny, hard and the adherence to the sapphire was good. The deposits were continuous and uncracked. At the higher temperatures there were significant differences. For instance, when the cooled sapphire disc was removed from the vacuum system in Run 3177-36 (626 - 642° C.), the deposit was a dull orange in color, completely transparent and uncracked. The surface was very smooth and appeared to reproduce the sapphire surface exactly. There was no obvious interaction between the coating and sapphire. The adhesion of the deposit to the substrate was good. However, scratching the edge of the deposit caused the deposit to be released. The deposit then changed instantaneously to black, opaque, wrinkled flakes. The flakes were approximately the same shape as when adhering to the sapphire--but they appeared to have increased slightly in area on being released.

Similar wrinkled flakes were produced in Run 3177-32 at 613 - 626° C. Although no transparent orange deposit was observed in this experiment, it is possible that it was produced during coating but changed to the black form during cooling. (See later discussion concerning quartz substrate).

The system consisting of the orange deposit and the sapphire substrate was apparently highly stressed. It is possible that the boron was similar to the rhombohedral form of boron described by Talley et al (6). It is not unlikely that the growth was epitaxial since the sapphire is also rhombohedral in form. On the other hand, there have been a number of reports of yellow, red and orange colored boron (7) (8). In any case, it was apparent that at about 600° C. sapphire had a significant effect on the type of boron deposited. In addition, it appeared likely that significant surface mobility of the boron would have been required to produce the type of deposit obtained.

2.4 Quartz

Fused quartz plates, 1.5 in. long, 0.5 in. wide by 0.080 in. thick were used as substrates in eight runs covering temperatures from approximately 300° C. to 750° C. In all, some 21 samples were produced. Quartz substrates with two surface conditions were used; one was highly polished, optically flat and transparent; the other was rough ground and optically opaque.

The results obtained from the coating experiments were as follows:

The typical deposit on the polished quartz surface was black and mirror-like at all temperatures tested. However, the degree of cracking was extensive. Since the coefficient of thermal expansion of quartz ($0.5 \times 10^{-6}/^{\circ}C$) is much less than that of boron, it is likely that the cracking resulted in a tensile failure of the boron during cooling after coating.

The adhesion of the boron to the quartz was generally excellent. In most instances, quartz fragments would adhere to the boron flakes when they were removed from the quartz substrate.

Although the adherence was excellent there was no other evidence of significant chemical interaction between the boron and quartz.

Coatings on the rough quartz surfaces reproduced the surface exactly. The coating then appeared dull and gray rather than the black and mirror-like deposit produced on the polished surfaces.

In Run 3177-32 (613 - 626° C.), a part of the boron deposit on the polished quartz specimen was orange in color and transparent. It appeared to be the same form of boron as produced on the sapphire substrates at 626 - 642° C. in Run 3177-34. Since the quartz was non-crystalline, it would appear that a rhombohedral substrate was not a necessary prerequisite for the formation of the orange form of boron.

In Run 3177-26 (704 - 713° C.) and Run 3177-27 (744 - 749), the polished surface of the quartz was scratched with a diamond pencil prior to coating. In the regions of the scratches, the boron tended to crystallize and form "whiskers" directed out from the surface of the substrate.

In Run 3177-27 (744 - 749° C.) it was noticed that about 10% of the area of the rough substrate had progressed to the stage of forming a dull brown "powder" above the normal gray deposit.

2.5 Boron Carbide

In Run 3177-26 (704 - 713° C.) two samples of boron carbide (B_4C)

were used as substrates for boron deposition. In both samples a part of the deposit was black, shiny, continuous and adherent. In the remainder, the deposit was dull, black and powdery. Similar combinations of continuous and powdery deposits were formed on the tantalum foil substrates in the same run. The powdery deposits on the boron carbide appeared identical to those formed on the tantalum, and also to those formed on the copper and silica substrates at higher temperatures. (See discussion concerning the copper and silica substrates above.)

These results confirmed that the powdery deposit formed at the higher temperatures on the tantalum substrate was not all tantalum diboride. Powder formation was initiated at about 700° C. by tantalum, copper and boron carbide substrates. Powder formation occurred on rough alumina surface at about 620° C. On the other hand, polished quartz and sapphire did not initiate powder formation in the boron deposit up to 750° C. These results suggest that SiO_2 and Al_2O_3 evaporated onto highly polished surfaces may be good barrier materials for the deposition of boron on tantalum at temperatures in excess of 750° C., but there was also evidence that the transparent orange form of boron would be formed. Since that form of boron was so highly stressed, it was considered an unlikely candidate for a high-strength material when deposited on the types of substrates practically available.

3. X-RAY ANALYSES

The X-ray work was divided into several parts. First, X-ray diffraction data were obtained for boron films deposited on a number of different substrates at temperatures covering the range of 105° C. to 749° C. The objective was to ascertain whether the substrate or substrate temperature had any effect on the degree of crystallinity of the boron films. In the second part of the work, X-ray diffraction patterns were obtained for the high strength--high modulus boron filaments (4 mil. diameter) which had been made by chemical vapor deposition onto 0.5 mil tungsten wire at approximately 1200° C. The data allowed direct comparison to be made between the vacuum evaporated boron film material and the high strength boron filaments.

The X-ray studies were performed on Siemens X-ray equipment which consisted of a Kristalloflex 4 generator, a horizontal tube stand with a fine focus copper X-ray tube and a type F diffractometer equipped with a NaI (Tl) scintillation counter with a 0.2 mm thick beryllium window. In order to minimize instrumental variability, all samples were evaluated using identical instrumental operative parameters, the only exception being recorder attenuation.

Two modes of sample preparation were utilized; the first consisted of mounting the specimen, as received, in a conventional holder. These specimens included both the boron filaments and the various boron coated substrates, such as tantalum, copper, quartz, sapphire and polyimide film. The second method of mounting was developed for those specimens which had been removed from the substrates in the form of flakes. This consisted of casting a thin (1 mil. thick) collodion substrate on water. The collodion film was then floated onto an X-ray holder, dried and the flakes hand positioned onto the substrate at the mid-line for maximum X-ray exposure.

The same set of X-ray holders were utilized throughout the study to minimize instrumental variability.

Consider first the series of experiments concerning the crystalline habit of boron filaments. Figure 1. is a typical X-ray scan. A number of scans were run on the filaments to ascertain whether filament orientation had any effect on the scan. No significant evidence of orientation was noted.

The scan obtained in Figure 1. was compared to powder diffraction patterns currently available for the tetragonal and rhombohedral forms of boron and for the tungsten borates and tungsten boride phases which have been indexed in the ASTM Powder Diffraction Data File.

The crystal form which most closely "matched" the pattern exhibited in Figure 1. was tungsten boride (WB_4) in the hexagonal crystal phase. The scan showed 12 peaks out of 21 present as coinciding with the WB_4 phase with an additional 4 peaks showing similarities to the tetragonal and rhombohedral phases of boron. These data are presented in Table III. In general, the relative intensity of the peaks indicated that the boron filaments contained relatively small amounts of crystalline boron. The major fraction of the boron was presumably "amorphous" to X-ray, although there was evidence of some boron crystallinity in the tetragonal and rhombohedral phases. The tungsten boride (WB_4) resulted from essentially complete interaction of boron with the tungsten core during the production of the filaments by chemical vapor deposition.

With the X-ray data of the boron made by chemical vapor deposition as a reference, a second series of samples were tested to examine both the degree of crystallinity and the nature of the phases of boron made by

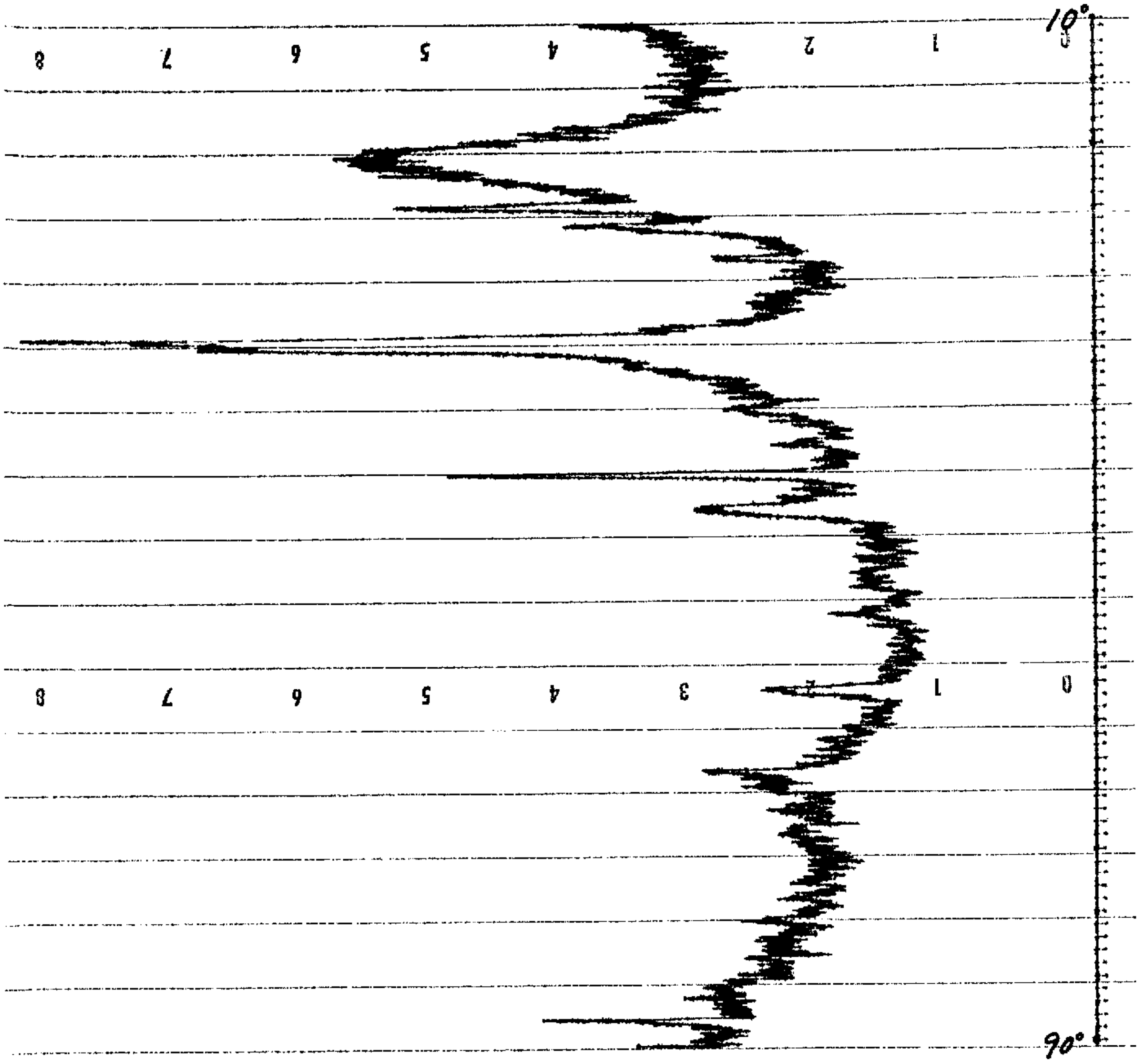


FIG. 1 X-RAY DIFFRACTION PATTERN

Material: Boron Filaments

Orientation: Parallel

Radiation: CuKa

Filter: Ni

Full Scale: 4 X 10^2

Tube Kv: 35

Tube Ma: 30

Detector Kv: 1.12

Aperture Slit: 1°

Detector Slit: 0.2 mm

Gon.: 2.5°/min.

Chart: 0.5 cm/min.

Rate: 1.25 cm/min.

Time Const.: 2 sec.

Scan Range: 10°-90° (20)

TABLE III

2θ ANGLES ($^{\circ}$)/"d" SPACINGS (A$^{\circ}$)

Boron Filaments		ASTM Diffraction Data File of Indexed Compounds which "Matched" Analyte		
Sample ⊥ To Beam	Sample //ℓ To Beam	B-12-469 Tetragonal	B-12-377 Rhombohedral	WB_4-19-1376 Hexagonal
20.7/4.21	20.7/4.28	20.3/4.37	20.8/4.25	
24.7/3.60	24.7/3.60			24.3/3.66
26.1/3.41	26.1/3.41			
28.6/3.12	28.6/3.12			28.3/3.15
34.9/2.57	34.9/2.57			34.7/2.58
35.5/2.53	35.5/2.53	35.4/2.53	35.2/2.55	
43.1/2.10	43.1/2.10		42.8/2.11	
45.5/1.99	45.5/1.99			45.3/1.99
48.1/1.89	48.1/1.89			47.8/1.90
56.4/1.63	56.4/1.63			56.1/1.64
58.6/1.57	58.6/1.57			58.4/1.58
62.3/1.51	62.3/1.51			62.0/1.50
68.7/1.36	68.7/1.36	68.6/1.36		
69.6/1.35	69.6/1.35			69.5/1.35
71.4/1.32	71.4/1.32			71.4/1.32
71.9/1.31	71.9/1.31			
73.1/1.29	73.1/1.29			73.9/1.28
80.1/1.20	80.1/1.20			79.8/1.20
85.5/1.13	85.5/1.13			
88.0/1.11	88.0/1.11			
88.3/1.10	88.3/1.10			

vacuum evaporation. These investigations involved samples in which the boron was analyzed both "in situ" on the substrate and also after removal as flakes. In all cases, a "blank" scan of the substrate material was made in order to eliminate those peaks associated with the substrate. The substrates which were analyzed are discussed below.

3.1 Boron on Tantalum

As shown in Table IV, X-ray data in the form of the 2θ angles were obtained both for boron on the tantalum foil substrate and for boron which had been removed as flakes. As the temperature increased from 105 - 258° C. to greater than 500° C., the number of peaks present also increased. This was more evident in the "flakes" although the boron on the tantalum substrate exhibited a similar trend.

3.2 Boron on Copper Substrate

The samples were prepared in essentially the same way as the boron-tantalum samples. The results of the X-ray analyses are shown in Table V.

The same effect was noted using the copper substrate as was evident from the tantalum substrate; namely, as the temperature increased, the number of peaks increased. However, the progression was not as uniform as in the boron-tantalum series as shown by the fact that three peaks were evident at 280 - 376° C. and five peaks present at 508 - 538° C. with no further increase in peak number as the temperature was raised to 749° C.

3.3 Boron on Quartz Substrate

This series consisted of boron evaporated onto polished quartz at

TABLE IV-A

BORON ON TANTALUM - 2θ ANGLES

BORON ON TANTALUM SUBSTRATE

Tantalum Foil (Substrate)	3177-38 307-374° C.	3177-36 400-450° C.	3177-35 600-621° C.	3177-32 612-626° C.
	20.6*			
34.9	35.0	34.9	34.9	35.0
				35.4*
39.1	39.1			39.1
50.5	50.1	50.0	50.1	50.5
56.3	56.0	56.0	55.9	56.0
60.5	60.5	60.5	60.5	60.5
62.8	62.3	62.3	62.3	62.7
				68.5*
69.9	70.0	70.0	69.9	69.5
* No. of Peaks not associated with substrate				
0	1	0	0	2

TABLE IV-B

BORON ON TANTALUM - 2θ ANGLES

BORON FLAKES--NO TANTALUM SUBSTRATE

Mounting Substrate (Collodion)	3177-33 105-258° C.	3177-30 400-433° C.	3177-29 508-534° C.
19.2	19.4		
	20.5*	20.5*	20.5*
		26.8*	26.8*
			27.0*
69.9	70.0	69.9	69.9
71.9	72.0	71.9	71.9
74.4	74.4	74.4	74.4

* No. of Peaks not associated with substrate			
0	1	2	3

TABLE V

BORON ON COPPER - 2θ ANGLES

Boron on Copper Substrate		Boron Flakes		
Copper Foil (Substrate)	3177-27 744-749° C.	Mounting Substrate (Collodion)	3177-21 280-367° C.	3177-29 508-534° C.
	19.4*	18.2		18.2
	20.0*		20.7*	20.1*
	28.2*		25.8*	25.8*
	28.7*		27.0*	26.8*
38.7	39.1			28.1*
43.7	43.7			28.6*
45.0	45.5	69.9	69.9	69.9
50.8	50.8	71.9	71.9	71.9
65.9		74.3	74.3	74.3
	74.2*			
90.0	90.1			

* No. of Peaks not associated with substrate

0	5	0	3	5

various temperatures. X-ray scans were made for samples of boron on the quartz substrate, only no flake analyses were made. Table VI summarizes the results. Only one very broad peak was present at all temperatures. This "peak" was also common to the quartz blank. The broad quartz peak was close to the normal boron peak which had a $2\,\theta$ angle of about 20.5°. Since the boron peak was broadened in many of the earlier samples because the boron was amorphous, it was not possible to separate the boron and quartz contributions at the lower angles. However, the absence of any peaks at the higher angles was significant. It appeared possible that the quartz tended to suppress crystal growth noted at the higher temperatures for other substrates.

3.4 Boron on Polyimide Film Substrate

A single scan was made for both the polyimide film and a boron-coated polyimide film made at $280 - 367^{\circ}$ C. The polyimide film appeared amorphous as characterized by a very large broad peak spanning some 12 to 14° ($2\,\theta$). The boron-coated film produced a similar scan.

3.5 Boron on Sapphire Substrates

The final series of scans involved boron evaporated onto sapphire discs. The results are also presented in Table VI.

Examinations of the X-ray scans showed only the presence of two peaks and these had the same $2\,\theta$ angles as the rhombohedral structure of boron. Of these two samples, the sample evaporated at $307 - 374^{\circ}$ C., appeared, if anything, to be slightly more crystalline than the 600° C. sample.

As a possible aid in ascertaining what effect the various substrates

TABLE VI

BORON ANALYSIS - 2θ ANGLES

SiO_2 Substrate	3177-24 626-642° C.	3177-26 704-713° C.	3177-27 744-749° C.	Sapphire Disc	3177-38 307-374° C.	3177-35 600+° C.
21.76	22.0	22.0	21.5	0	35.5	35.5
				0	43.2	43.4

No. of Peaks not associated with substrate

0	0	0	0	0	2	2

and/or temperatures might have on the crystallite size of the boron, a crystallite index was used for the two substrates that showed the greatest change in peak dimension at a given 2 θ angle versus temperature. The two substrates used were tantalum and copper.

The index is based on the Scherrer (9) equation for the mean dimension of crystallites. The equation states:

$$D = \frac{K\lambda}{\beta\,(\text{radius})\cos\theta}$$

where K = a shape constant approximately equal to unity and for this study assumed to be 1.

λ = wavelength (A^{o})

β = angular width at half maximum intensity amplitude.

When the equation was applied to the data obtained for the B/Ta and B/Cu substrates at varying temperatures, the following results were obtained.

Crystallite Size Index

$2\theta = 20.5^{o}$

Substrate & Temp. ^{o} C.	Width at 1/2 Max. Intensity-cm.	Crystallite Size A^{o}
Boron Filaments	4.3	20
B/Ta @ 105-258^{o}	6.2	14
B/Ta @ 307-374	3.4	25
B/Ta @ 400-433	3.1	28
B/Ta @ 508-534	3.4	25
B/Ta @ 613-626	0	0
B/Cu @ 280-267	2.4	35
B/Cu @ 508-534	3.4	25
B/Cu @ 749-774	0.3	283

The above data imply a relationship between the crystallite size or structure (order) and temperature. For example, the B/Cu (749 - 774° C.) specimen showed the largest crystallite size implying a near perfect crystalline order. In contrast, the B/Ta (105 - 258° C.) specimen exhibited the smallest crystallite size implying a disordered structure (irregular lattice spacing, dislocations, etc.). These observations are derived from the parameter: "width at 1/2 maximum intensity amplitude" of the peak at 20.5° (2θ) on the diffraction pattern. As the width increases, the crystallite size as well as the crystalline order decreases. Conversely, narrow peaks would indicate a large crystallite size and ordered structure.

The crystallite index indicated that if boron was evaporated onto a tantalum substrate at a temperature greater than 300° C., the crystallite size and order would approximate that of the boron filaments. If copper is utilized as the substrate, the evaporation temperature should be around 500° C. to approximate the boron filaments. A temperature of 750° C. resulted in a much larger crystallite size, approximately 11 times as large, with a very ordered structure.

In summary, the X-ray diffraction studies of the boron samples indicated the following:

> The boron filaments appeared to be largely amorphous boron whose major crystal impurity was tungsten boride (WB_4) in the hexagonal phase. Traces of tetragonal and rhombohedral boron were present.
>
> The effect of increasing the substrate temperature during condensation on tantalum showed that a low temperature (105 - 258° C.) produced crystallites of a small size and disordered structure. Temperatures between 300° C. and 534° C. resulted in increased

crystallite size and order above that of the filaments. High temperatures produced "amorphous" boron with evidence of some tetragonal boron formation. In addition, the 27.0° peak in Table IV-B could not be associated with any of the known boron peaks. It is, however, an assigned peak for Ta_3B_2; and, hence, probably indicates boron-tantalum interaction.

The temperature effects of boron on copper showed that material subjected to elevated temperatures (749 - 774° C.) produced very large crystallites with highly ordered structure. Temperatures of 534° C. or lower produced crystallites and order similar to that found in the boron/tantalum specimen at the same temperatures.

The influence of substrates on the boron crystallite size and order showed that copper appeared to affect these two properties more than the tantalum. The other substrates (silica, sapphire and polyimide) were not suitable for evaluating this parameter.

4. DENSITY MEASUREMENTS

According to Talley (10) the density of amorphous filamentary boron made by chemical vapor deposition from boron tetrachloride on tungsten is 2.35 g/cc. The density was measured after removal of the tungsten core. The temperature at which the boron was produced was not specified but it was likely to be in the range of 1100 - 1300° C. Talley has also indicated that the strength of the filament was a strong function of the temperature at which it was made.

The purpose of this phase of the present program was to measure the density of boron made by vacuum evaporation and to ascertain whether the density was affected by:

The substrate temperature during deposition

The chemical composition of the substrate.

The boron samples used for density measurement were selected from the deposition runs summarized in Table I. In order to obtain satisfactory samples, several conditions were required. First, it was necessary that the boron not be contaminated by the substrate. In those cases where there was no chemical interaction between boron and the substrate, adhesion was generally poor and physical removal of boron flakes was easily accomplished. This situation typically occurred at the lower deposition temperatures. However, there is also interest in measuring the density of boron deposited on substrates held at higher temperatures. And here the likelihood of chemical interaction was greater--and the certainty of complete removal of the substrate and possible chemical interaction products less certain. The use of release agents such as boron nitride was tried but interaction with the so-called release agent was still a possibility. Removal of boron from a copper substrate was relatively straightforward. In general, the adhesion was poor--and a diluted nitric acid wash removed any adhering copper. Polyimide film could be removed efficiently by hydrolysis of the film in warm 20% caustic soda. An aqueous solution of hydrazine was also effective. Removal of boron from tantalum, quartz and sapphire was more difficult. In general, flakes which had been physically split from the surface were considered more reliable.

The method of density measurement was similar to that used by Talley. Density columns of various ranges of density were set up by mixing varying amounts of dibromomethane (2.49 g/cc) and ethylene dibromide (2.18 g/cc). In all, three columns were made. The density ranges used were 2.30 - 2.35 g/cc, 2.27 - 2.36 g/cc and 2.16 to 2.34 g/cc. Each column was thermostatically controlled at $25.0^{\circ} \pm 0.2^{\circ}$ C. The density values of the mixed fluid were determined at 4 or 5 heights in the column by the equilibrium positions of small calibrated glass floats with densities of 2.3000 g/cc, 2.3200 g/cc, 2.3400 g/cc, 2.3500 g/cc, and 2.3600 g/cc.

Small boron flakes--approximately 0.1 in. by 0.1 in. with a thickness of 0.1 mil. were cleaned in diluted nitric acid, distilled water, and trichlorethylene. The flakes were then boiled under vacuum in ethylene dibromide to remove any adhering gas and transferred wet into the density column. The density of the flakes was estimated by allowing the flake to establish its equilibrium height and then linearly interpolating on the basis of the heights of the calibrated density floats.

The results are summarized in Table VII and Figure 2.

The most significant results were:

TABLE VII

SUMMARY OF DENSITY DATA

Run No.	(°C) Temperature Range	(°C) T_{av}*	Substrate	(g/cc) Density
3177-40	40-147	120	PI	2.20
3177-40	40-147	120	Cu	2.300
3177-40	40-147	120	Ta	2.320
3177-39	75-164	142	PI	2.300
3177-39	75-164	142	Cu	2.232
3177-39	75-164	142	Ta	2.296
3177-33	105-258	220	PI	2.238
3177-33	105-258	220	Cu	2.296
3177-41	246-294	282	PI	2.32
3177-41	246-294	282	Cu	>2.32
3177-41	246-294	282	Ta	2.32
3177-31	280-367	345	PI	2.330
3177-31	280-367	345	PI	2.283
3177-31	280-367	345	PI	2.342
3177-31	280-367	345	Cu	2.311
3177-31	280-367	345	Cu	2.326
3177-31	280-367	345	Ta	2.317
3177-42	367-414	403	PI	2.32
3177-42	367-414	403	Cu	>2.32
3177-42	367-414	403	Ta	>2.32
3177-30	400-433	424	Cu	2.295
3177-30	400-433	424	Ta	2.309
3177-30	400-433	424	Ta	2.323
3177-29	508-534	525	Cu	2.347
3177-29	508-534	525	Cu	2.357
3177-29	508-534	525	Ta	2.288
3177-29	508-534	525	Ta	2.295
3177-32	613-626	621	Sapphire	2.294
3177-32	613-626	621	Sapphire	2.284
3177-26	704-713	710	Cu	2.297
3177-26	704-713	710	Cu	2.291
3177-26	704-713	710	Quartz	2.280
3177-26	704-713	710	Quartz	2.294

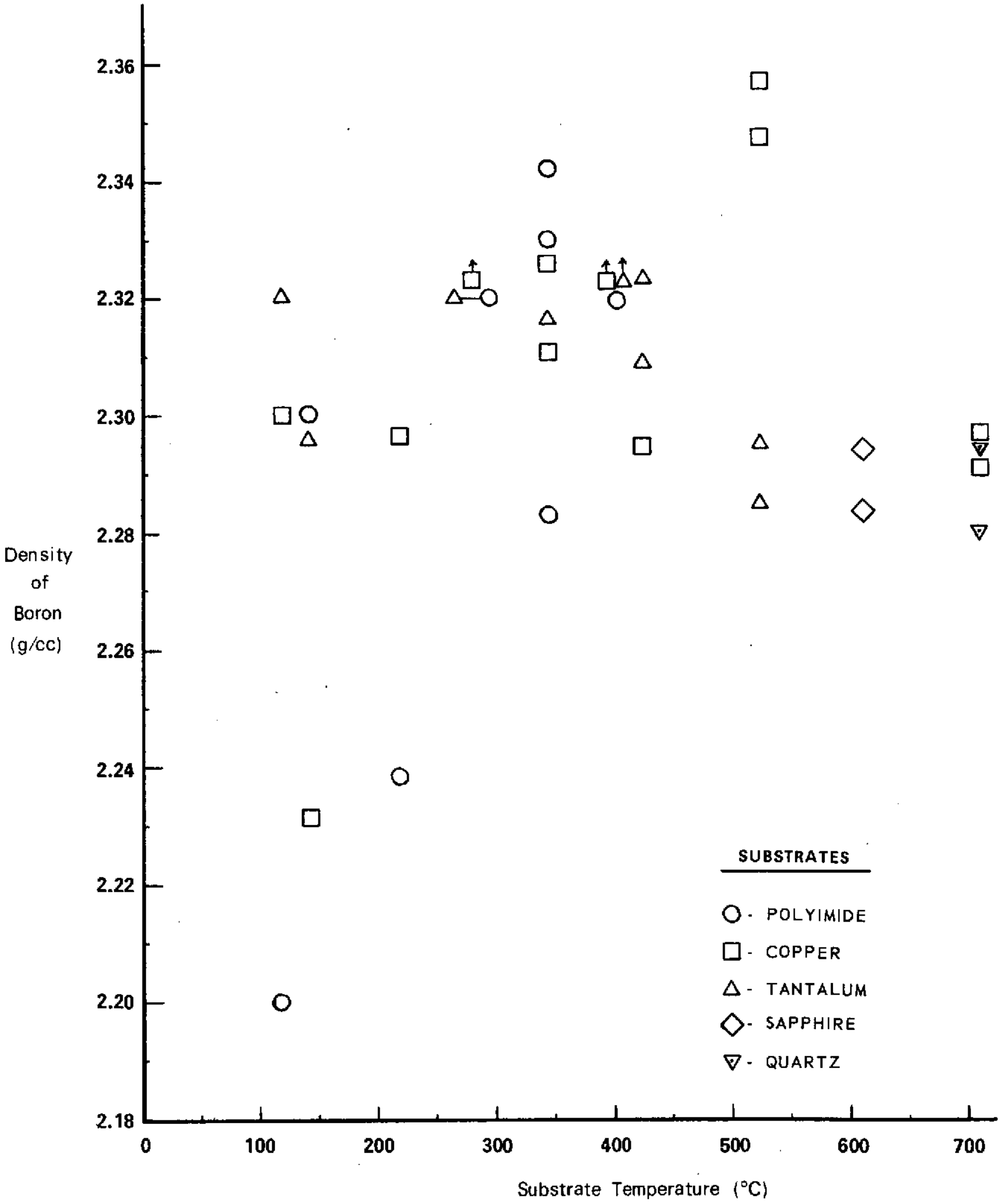
---

* Since the temperature of the substrate rose most rapidly at the beginning of a run when the shutter was opened, an estimate of the time average temperature was made according to:

$$T_{av} = 0.25\ T_{min} + 0.75\ T_{max}$$

FIGURE 2

VARIATION OF BORON DENSITY WITH TEMPERATURE



The samples of vacuum-evaporated boron showed large differences in density. The lowest value measured was 2.200 g/cc while the highest density was 2.357 g/cc. The low density material was formed on polyimide film substrate at an average temperature of about 140° C. The high density material was formed on a copper substrate at 525° C.

Although there was considerable scatter in the data, there appeared to be an increase in density with deposition temperature for both the polyimide substrates and the copper substrates up to 525° C. The density values for the boron deposited on tantalum showed less variation with temperature than either the polyimide or copper and, if anything, the density decreased with temperature.

The densities of deposits formed at 620° and 710° were between 2.28 and 2.30 g/cc--significantly lower than the maximum value of approximately 2.35 g/cc.

In general, the flakes used for density measurement decreased in size as the formation temperature increased. The samples for the 600 and 700° C. measurements were very small, and in all likelihood had undergone changes in physical dimensions (and therefore density) on being removed from the substrates.

The above density data indicated that relatively high substrate temperatures were required to produce boron with a density approaching 2.35 g/cc; but high temperatures did not guarantee high densities. Since the X-ray and morphology work in the current program had indicated a pronounced tendency for crystallographic change at temperatures in excess of 550° C., it is possible that the lower densities measured for the high temperatures were values which did not pertain to 100% amorphous boron.

In addition, it is likely that relief of the compressive stresses occurred when the boron was removed from the substrate. The free flake would then have a lower density than when bonded to the substrate.

The fact that the earlier work showed that tantalum tended to promote crystallization of the boron may explain the large difference in the densities of boron prepared at 525° C. on the copper and tantalum substrates.

5. STRENGTH OF DEPOSITS

The work on the strength of boron film deposits in the current program was essentially a continuation of the work reported in the earlier NASA program, NASW 2094 (3). The results obtained in that program had indicated that the strength of boron films deposited on tantalum increased as the substrate temperature was increased over the range from 385° C. to 600° C. Temperatures in excess of 600° C. produced deposits which had much lower strengths, and this was attributed to the formation of tantalum diboride at the higher temperatures. The maximum strength reported in NASW 2094 was 270 x 10^3 psi. As outlined earlier in this report, work in the current program showed that the low strength of the boron deposited on tantalum at temperatures in excess of 600° C. was attributable to a transition from amorphous boron in a continuous film form to "powdered" crystalline boron. It was possible that crystallization was promoted by some tantalum boride formation. The strong tendency for the formation of crystalline forms of boron at the higher temperatures suggested that the work on the measurement of strength should be restricted to the lower temperatures where the preparation of amorphous films was more certain. The main aims of the current program were:

Improve the method for the direct measurement of the strength of thin boron films deposited on thin metallic substrates.

Make further measurements of the strengths of boron films made under controlled temperature conditions.

Ascertain whether the thickness of the boron deposits had any effect on strength.

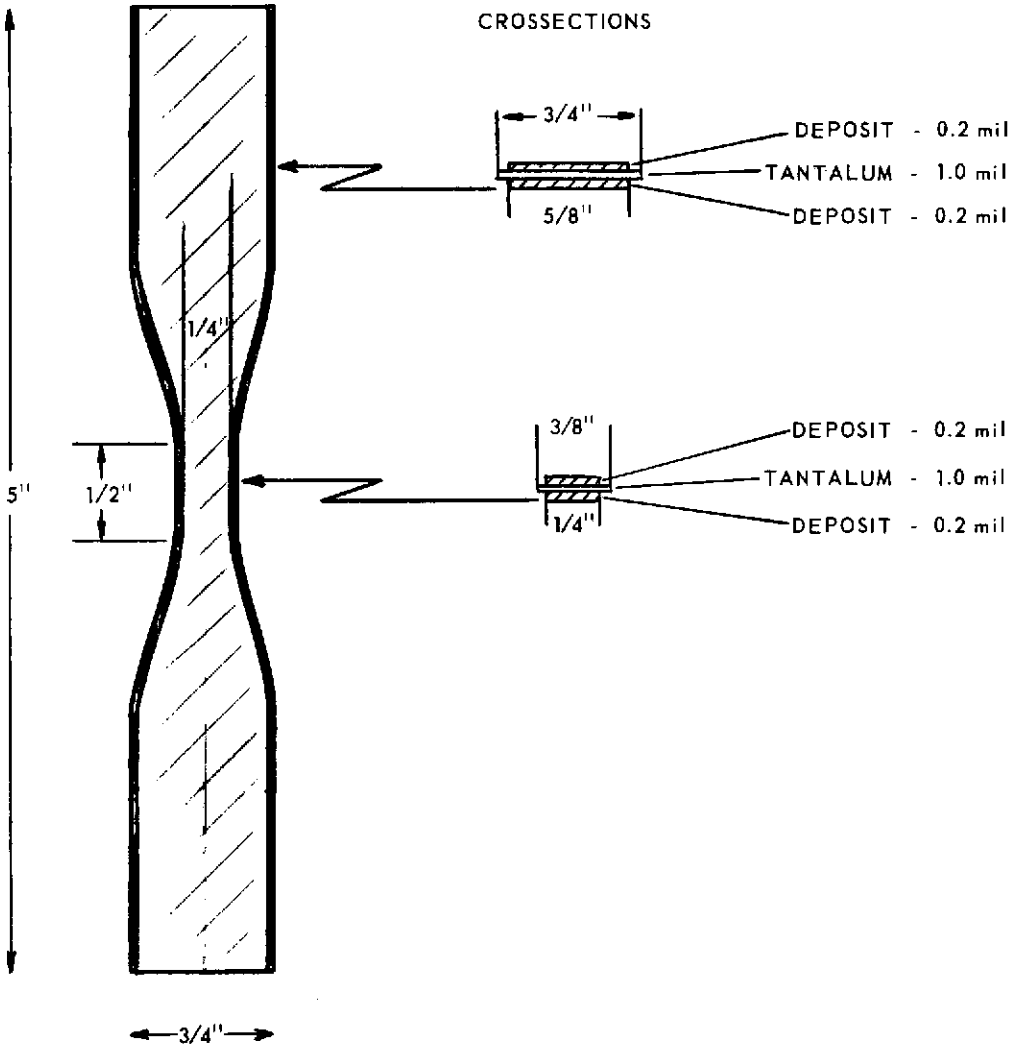
During work on Contract NASW 2094, 3/4 in. wide tantalum foil was used as a substrate and this was coated on both sides with boron through a mask using a flip-flop procedure (3). In the flip-flop procedure, the substrate (and masks) were rapidly rotated through 180° every 10 seconds so as to build up the coating on both sides of the substrate at the same rate. This procedure produced flat tensile specimens whereas a very wrinkled specimen was formed when first one side was coated and then the other.

In the 2094 work, two mask shapes were used. The first produced a 1/2 in. wide strip of boron on both sides of the 3/4 in. wide tantalum substrate. In the second case, the mask was shaped to produce a boron deposit which was necked down to 3/8 in. wide in the center of the specimen. Strain gauges (1/8 in. x 1/8 in.) were mounted on this reduced area section of boron. In the 2094 work, many specimens failed in the grip areas and not in the region of the strain gauge. However, the necked specimen represented an improvement. In the current program, further efforts were made to reduce the frequency of grip failure. Several changes were made. In the first instance the tantalum substrate was made into a dogbone shape rather than having parallel sides as in NASW 2094. This dogbone was then masked to produce a dogbone strip of boron on both sides of the tantalum with the width of the boron always being less than the width of tantalum. The dimensions of the resulting tensile specimens are shown in Figure 3. The strain gauges--one each side--were mounted in the center section where the evaporated deposit had parallel sides for about 1/2 inch.

A further refinement related to the strain gauges. The gauges, Type FAE-25S-12-S6 made by Baldwin; Lima and Hamilton, measured 1/8 in. x 1/8 in., but with coating and backing they were comparable in thickness to the tensile specimen. In order to reduce the strengthening effect of the gauges, 2 mil polyimide film was bonded to both sides of

FIGURE 3

TENSILE SPECIMEN DESIGN



the tensile specimen in all regions except that occupied by the strain gauges. Care was taken to use very small amounts of epoxy and Eastman 910 adhesives for these bonding operations.

Although these procedures were painstaking and time consuming, they were necessary to achieve a high proportion of tensile failures in the region of the strain gauges. In the instances where failure did not occur at the strain gauges, the failure could generally be traced to a major flaw elsewhere in the test specimen.

Usually five specimens were mounted in the flip-flop mechanism for each coating run. Normally one of the specimens was masked completely so that it remained uncoated for the run, but experienced similar handling and temperature conditions. Testing of the uncoated sample gave base data concerning the stress-strain characteristics of the substrate. The effects of the coating could then be more accurately determined.

Before mounting in the coater the tantalum substrate was polished and cleaned as follows:

The specimen was oriented so that the rolling marks in the foil were lengthwise in the specimen. The center one inch of the substrate was then polished on both sides with the following silicon carbide papers: 320 grit, 400 grit, 600 grit, 2/0 grit. Kerosene was used for the 2/0 paper, while water was used for the three coarser papers. The substrate was then chemically polished for 5-7 minutes with a mixture made up of 60% lactic acid, 20% nitric acid and 20% hydrofluoric acid. The substrates were then thoroughly washed with water, ethanol, acetone and finally with ethanol again. The samples were then weighed and mounted in the flip-flop holder for insertion into the vacuum evaporator.

The vacuum evaporator used in the current program was different from that used under the earlier NASW 2094 contract. Several requirements dictated the change. The evaporator used in NASW 2094 had a single crucible source and an input power limit of 10 KW. One of the aims of the present program was to ascertain whether the strength of a boron deposit was dependent on the thickness of the deposit. The planned approach was to measure the strengths of a series of boron deposits all having the same total thickness but made up of one, two, four and eight layers of boron each interspersed with a layer of vacuum evaporated tantalum. And preliminary work established that 10 KW was insufficient power to evaporate tantalum at a reasonable rate.

The evaporator (System 421) used in the current work had a Pierce type gum with usable power in excess of 30 KW. Two water-cooled copper crucibles were available. The boron crucible was approximately 15 inches from the substrate to be coated while the tantalum source was about 11 inches below the samples. Before coating, the samples were rotated in an electrically heated oven to obtain the desired degree of preheat. Temperatures were measured by a thermocouple exposed to the same radiant environment as the substrates to be coated. Because of the radiation from the sources--particularly the tantalum--it was not possible to maintain constant substrate temperatures during evaporation. Typically, the temperature rose very rapidly at the outset of exposure of the sample to the vapor stream. This was particularly the case if the substrate temperature were initially low. The rate and magnitude of the rise was then substantial--in excess of 100° C.

The main conditions for those runs involving the consecutive evaporation of tantalum and boron are summarized in Table VIII. Runs were made in which 1, 2, 4 and 8 layers of boron were applied to both sides of the substrate. In each case a layer of tantalum equivalent to half a boron layer was

TABLE VIII

CONSECUTIVE EVAPORATION OF TANTALUM AND BORON

GENERAL CONDITIONS

SUBSTRATE:	Tantalum Foil (1 mil thick)	
TENSILE SPECIMEN:	Masked Dogbone ①	
TANTALUM EVAPORATION:	20 KW	8 min. (Total) ②
BORON EVAPORATION:	20 KW	16 min. (Total)

RESULTS:

Sample No.	No. of Layers Ta	No. of Layers B	Temperature (°C)	Proportional Limit Strain (%)	Estimated Strength (KSI) ③
42-348-1	2	1	511-555	0.14	84
42-349-1	2	1	400-485	0.08	48
42-349-2	2	1	400-485	0.14	84
42-350-1	5	4	414-480	0.05	30
42-350-2	5	4	414-480	0.08	48
42-351-1	9	8	395-508	0.13	78
42-351-2	9	8	395-508	0.20	120
42-355-3	5	4	253-395	0.14	84
42-355-4	5	4	253-395	0.14	84
42-356-2	3	2	393-527	0.15	90
42-356-4	3	2	393-527	0.18	108

① Except 42-348-1 Tensile sample was straight sided

② Except 42-348-1 Tantalum evaporation 5 min.
Boron evaporation 10 min.

③ Assumes modulus of boron = 60×10^6 psi deposited before the first layer of boron and after the last layer of boron. Consequently, one extra layer of tantalum was deposited in each case; but the first and last were half thicknesses.

The temperatures during deposition covered the range of 253 - 555° C. In general, attempts were made to keep the pressure below 1×10^{-5} torr during coating. While this was possible during the evaporation of boron, pressures in excess of 2×10^{-4} torr were experienced in evaporating the tantalum.

The highest pressures occurred in Runs 42-348 and 42-349. It appeared that the tantalum required extensive degassing because in Run 42-351 the pressures during tantalum evaporation decreased during the run to values of approximately 2×10^{-6} torr.

After coating, the samples were allowed to cool--generally overnight in vacuum. They were then removed from the substrate holder and weighed.

Despite considerable care taken in premelting and degassing of both the boron and the tantalum, it was apparent that many of the samples prepared were severely damaged by spits from the melt. It was also apparent that the tendency for spit damage increased with the number of layers. Since each layer required a separate melting-in operation, it is possible that increased damage resulted from the greater exposure to spitting associated with the earlier periods after each melt-in.

Those samples which were not severely damaged were instrumented with strain gauges and the load-strain characteristics measured in an Instron Tensile Machine operating at a strain rate of 0.02 in./min. The proportional limit strain was obtained from the load-strain curve. It was then assumed that the proportional limit strain represented the failure strain of the boron film. An estimate of the boron strength was then obtained assuming the boron to have a tensile modulus of 60×10^6 psi.

As shown in Table VIII, the highest strength estimated for this work with tantalum was 120 KSI. The range of strengths was 30-120 KSI. There did not appear to be any correlation with either the number of layers or with the temperature during deposition. Independent measurements of the proportional limit strain for the uncoated tantalum showed it to be in excess of 0.30%. The boron-tantalum consecutive deposits were obviously brittle and not strong.

Microscopic examination of the tantalum deposits did not indicate significant interaction with the boron, but it was apparent that the deposited tantalum was very hard and brittle. It did not have the ductility of the substrate. It was concluded that the tantalum has either reacted to some extent with the boron or with the residual gases in the vacuum system. The high melt temperature of the tantalum (3000° C.) combined with the high mass of the vaporized atom could well combine to promote excessive energy transfer at the substrate on condensation.

In an attempt to overcome some of these difficulties, a restricted series of runs using titanium as the evaporant, rather than tantalum, was carried out in the latter stages of the program. The main conditions are outlined in Table IX.

In this series, tantalum foil was again used as the main substrate. The first layer deposited onto the tantalum was titanium with a thickness of about 1/2 the average thickness of the subsequent layers of titanium. Each boron layer was interspersed with a layer of titanium. The final coating

TABLE IX

CONSECUTIVE EVAPORATION OF TITANIUM AND BORON

GENERAL CONDITIONS

SUBSTRATE:	Tantalum Foil (1 mil thick)	
TENSILE SPECIMEN:	Masked Dogbone	
TITANIUM EVAPORATION:	9 KW	16 min. (Total)
BORON EVAPORATION:	20 KW	16 min. (Total) ①

RESULTS:

Sample No.	No. of Layers Ti	No. of Layers B	Temperature (°C)	Proportional Limit Strain (%)	Estimated Strength (KSI)②
42-357-2	5	4	367-426	0.39	234
42-357-4	5	4	367-426	0.38	228
42-370-1	5	4	285-343	0.17	102
42-370-3	5	4	285-343	0.21	126
42-371	9	8	300-367	0.14	84
42-372-2	5	4	273-324	0.10	60
42-372-4	5	4	273-324	0.14	84
42-373-1	9	8	271-319	0.22	132
42-373-3	9	8	271-319	0.14	84
42-373-4	9	8	271-319	0.13	78

① Except 42-372 Boron 17.5 KW 24 min.

Except 42-373 Boron 18.0 KW 24 min.

② Assuming modulus of boron 60 x 10^6 psi was another half thickness of titanium. The volume fraction of boron in the evaporated deposit was about 0.25.

The titanium evaporation process worked very satisfactorily. The titanium deposits were adherent and ductile. The advantages of using titanium for the consecutive deposition were obvious. The lower melting point of titanium (1670°C.) and the higher vapor pressure (1 torr at 2200° C.) compared to tantalum resulted in lower temperature increases during coating. (The melting point of tantalum is 3000° C., and it has a vapor pressure of 1 torr at 3530° C.) In addition, lower pressures were attainable during evaporation. The range of temperatures used in the series was from 271° C. to 426° C. These lower temperatures were chosen to minimize the possible effects of excessive boron-titanium interaction. In all runs there were samples which were severely degraded by spits from the melt. Spitting was more likely to occur early after melt-in, and although melt-in was carried out with a shutter screening the deposit, the multiple layers approach precluded long evaporation times for each melt. The four-layer boron deposits required nine melt-ins--four for boron and five for titanium--while the eight boron layers required 17 melt-ins.

In several instances, the tantalum-boron-titanium samples were impacted by a larger droplet of boron. The ensuing exothermic reaction was sufficient to rapidly convert the sample to tantalum and titanium borides. However, in those cases where the samples were not impacted by large boron droplets, the deposits were smooth, shiny, flat and uncracked. The intermediate titanium layers were ductile and no boron-titanium interaction layers were apparently on examination under the optical microscope. The samples which did not have large flaws were tested in a manner similar to that described for the earlier tantalum-boron series. The results are included in Table IX. The results in this series were of interest for several reasons. First, within any one run, the degree of agreement between samples was relatively good--certainly as good as has been achieved in any of the earlier work on these programs. For instance, in Run 42-357, Samples 2 and 4 had proportional limit strains of 0.39% and 0.38% respectively. Samples 2 and 4 in Run 42-372 had proportional limit strains of 0.10 and 0.14% respectively.

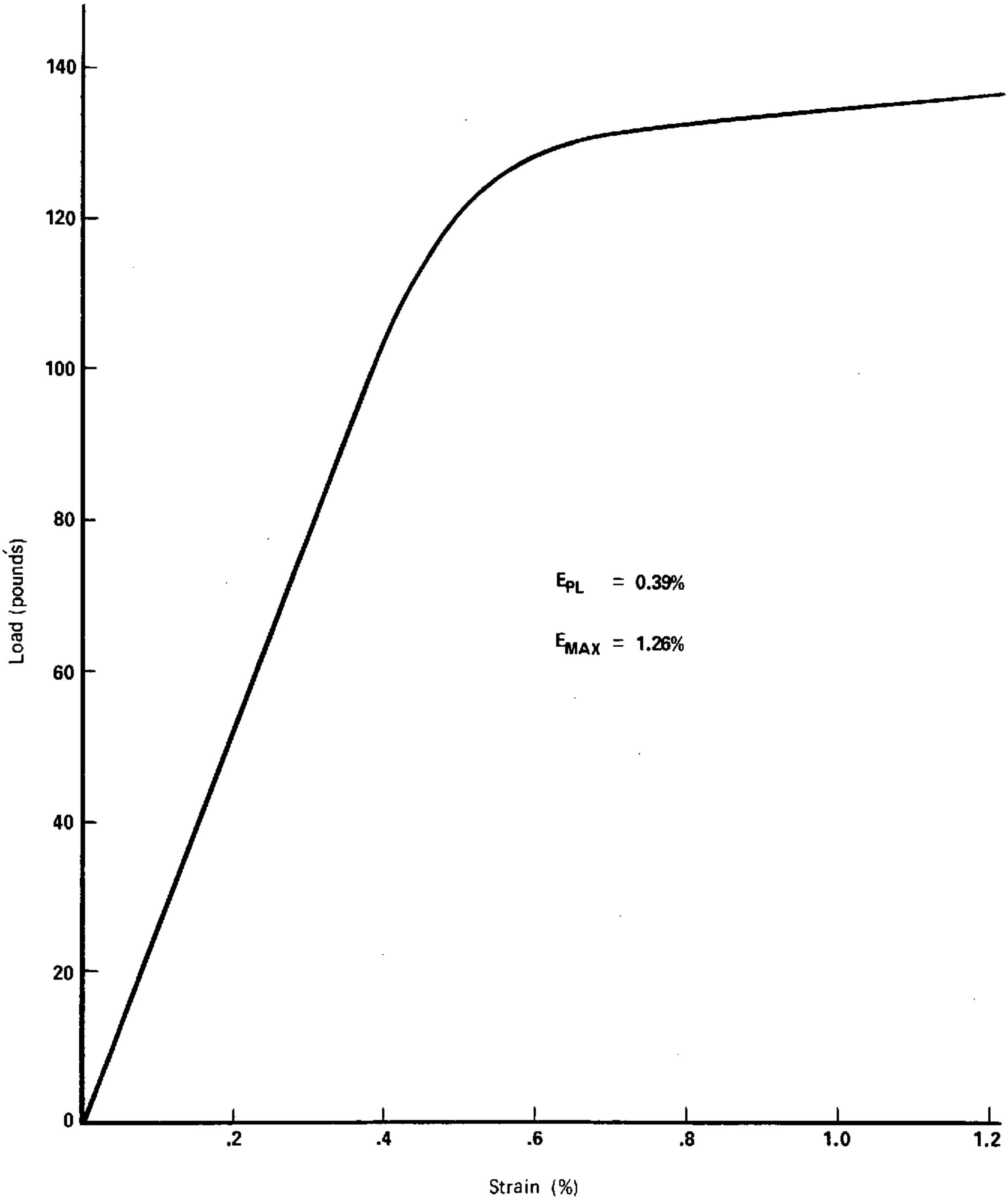
The proportional limit strain of 0.39% obtained for Sample 42-357-2 was the highest obtained in this program. Assuming the boron to have a modulus of 60×10^6 psi, the strain represents a strength of the boron film of 234×10^3 psi. The load-strain curve for this sample is reproduced in Figure 4.

Figure 5 is an electron micrograph of Sample No. 2 from Run 42-357 after tensile testing. The tantalum substrate is shown in the center of the figure. On each side there are five layers of titanium and four layers of boron. Figure 6 is section at higher magnification--1500 X. Several points should be made. First, there does not appear to be significant interaction between the titanium and boron. Second, the imperfections in the substrate are reproduced by the deposit. In Figure 6, the depth of the imperfections in the substrate are comparable to the thickness of the boron deposit. Tensile cracks in the boron are clearly visible. While the cracks do not coincide with the imperfections caused by the roughness of the substrate, it is possible that the cracks were initiated at a plane other than that photographed. In any case, it would appear necessary to develop better substrate polishing techniques than used on the sample photographed.

As shown in Figure 5, in Run 42-357, samples with four layers of boron were formed on each side of the tantalum substrate. The average thickness of the boron layers was approximately 0.09 mil. The temperature during

FIGURE 4

LOAD-STRAIN TRACE FOR SAMPLE 42-357-2



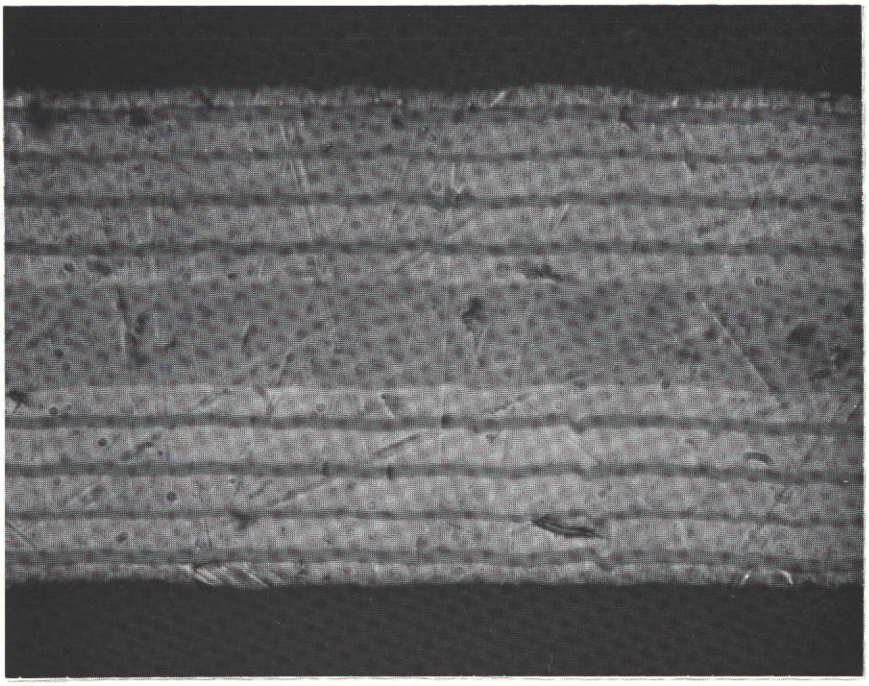


FIG. 5 SECTION TENSILE SPECIMEN 42-357-2 **750X**

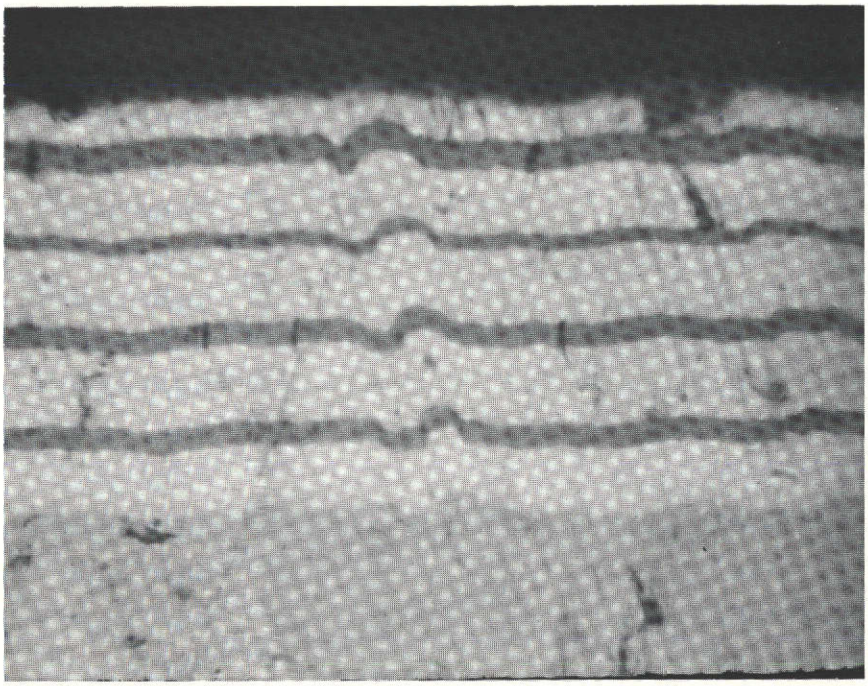


FIG. 6 SECTION TENSILE SPECIMEN 42-357-2 **1500X**

deposition was 367 - 426° C. Other four-layer deposits made at lower temperatures gave lower proportional limit strains. Samples from Run 42-370 made at 285 - 343° C. averaged 0.19% strain, while samples from Run 372 made at 223 - 324° C. averaged 0.12% strain. These results suggest that lower strength boron was produced at the lower temperatures. The data do not show that higher strength results from a larger number of layers each with a smaller boron thickness. It is possible that the effects of layer thickness were overshadowed by the influences of temperature and other variables such as spit defects, substrate morphology, etc. The results of earlier work in this program concerning the relationship between the density of the deposit and the deposition temperatures indicated that temperatures of at least 400° C. were necessary to produce "fully dense" deposits.

It was interesting to note that a failure strain of 0.38% could be produced at a temperature as low as 400° C. The highest failure strain obtained in the earlier program NASW 2094 was 0.44% for a sample produced at 602 - 618° C. with single layers of boron on each side of a tantalum substrate. At 600° C. the titanium would have undoubtedly interacted with the boron. The highest failure strain measured in NASW 2094 at 400° C. was less than 0.2%. The comparison suggested that adherent and relatively strong deposits could be made at 400° C. by using consecutive deposition.

The interest in using temperatures approximating 400° C. rather than 600° C. stems from the advantages that accrue in terms of strength to weight and stiffness to weight if a low density plastic substrate could be used instead of a denser metal. Polyimide films can be vacuum coated up to about 400° C. Small samples of polyimide film were included in some of the runs summarized in Table IX. It was very difficult to hold small pieces of 0.5 mil polyimide film flat during the coating and no tensile specimens were obtained. However, small sections of the consecutive titanium-boron deposits produced in Run 42-373 at 271 - 319° C. were shiny, adherent and uncracked. Samples coated in Run 42-370 up to 343° C. were partially destroyed by spit ignition of the boron-titanium deposit, but the remaining material showed that consecutive deposition of boron and titanium was possible on a polyimide substrate at temperatures in excess of 325° C. Further work on boron-titanium deposits using a polyimide substrate appears warranted.

During the course of the experimental work in the program, a large number of scanning electron micrographs were taken to examine the morphology of the deposits, type of defects, etc. A number of these samples were taken from tensile specimens. The predominant cause of tensile failure was a defect which appeared to be caused by a spit or molten droplet of boron impacting the deposit. Also during the program, a number of small strips of coated substrate (1 in. long by about 0.1 in. wide) were bent around mandrels to measure the failure strain in bending. In these cases, the point of crack initiation generally could be traced to a flaw caused by a droplet. (More detailed information on the morphology of the deposits and defects is presented in the next section of this report.) Since the flaws caused by droplet impact covered a very large range of sizes, the effects of droplets on the tensile strain values obtained were also undoubtedly great and probably overriding in most cases. For this reason, separating out the effects of temperature and layer thickness remained a difficult problem.

Nevertheless, the work in this program confirmed that further progress on increasing the strength of vacuum deposited boron films requires the following:

Elimination of spits and droplets issuing from the melt and impacting the deposit.

Defect-free (smooth and clean) substrates.

Strict control of the actual temperature of the substrate and deposit during deposition.

6. MORPHOLOGY OF DEPOSITS

In the course of the present program many optical, electron and scanning electron micrographs were taken to investigate the effects of the following variables on the morphology of the boron deposits:

Temperature of deposition

Composition of substrate

Morphology of substrate

Nature of defects

The scanning electron micrographs in the following series of figures (Figures 7 through 20) have been selected to illustrate some of the more important results.

Figure 7 is a micrograph of boron deposited on a tantalum substrate held at 602 - 621° C. in Run 317--35. The magnification is 2050 X. Several features are important. First, the deposit reproduces the rolling marks and surface roughness in the substrate, but there is also evidence that at 602 - 621° C. some "graininess" had developed in the deposit. This is shown more clearly in Figure 8 which is the same deposit at a magnification of 10,200 X.

Also shown on Figure 7 are a number of surface growths or deposits. At higher magnification these deposits were shown to be made up of a collection of platelets growing out of the surface of the boron deposit. The nature and general structure is shown more clearly in Figures 9 and 10. Figure 9 is

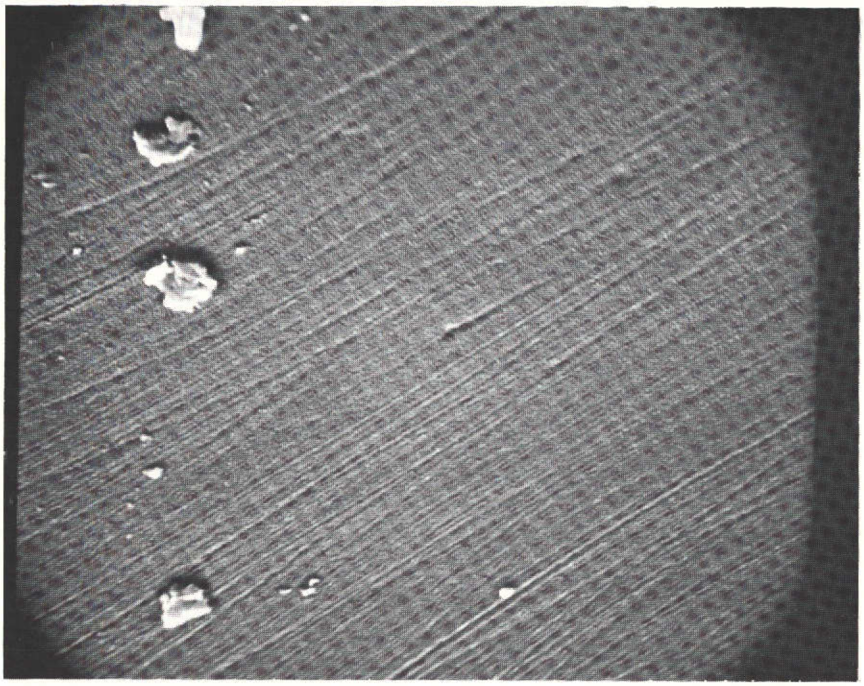


FIG. 7 BORON ON TANTALUM - 602 - 621 °C **2050X**

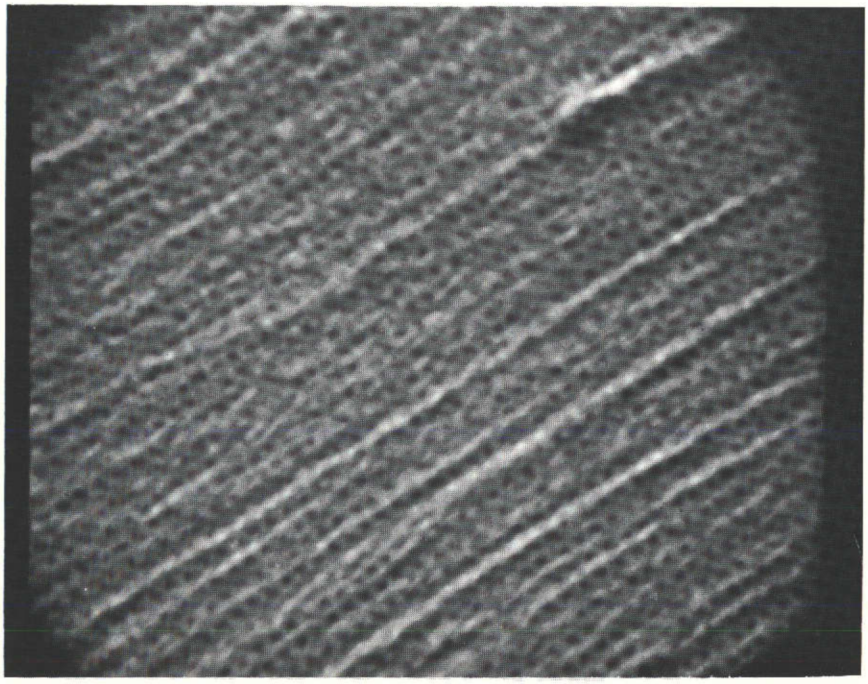


FIG. 8 BORON ON TANTALUM - 602 - 621 °C **10,200X**

FIG. 9 BORON GROWTH ON TANTALUM - 704-713°C **950X**

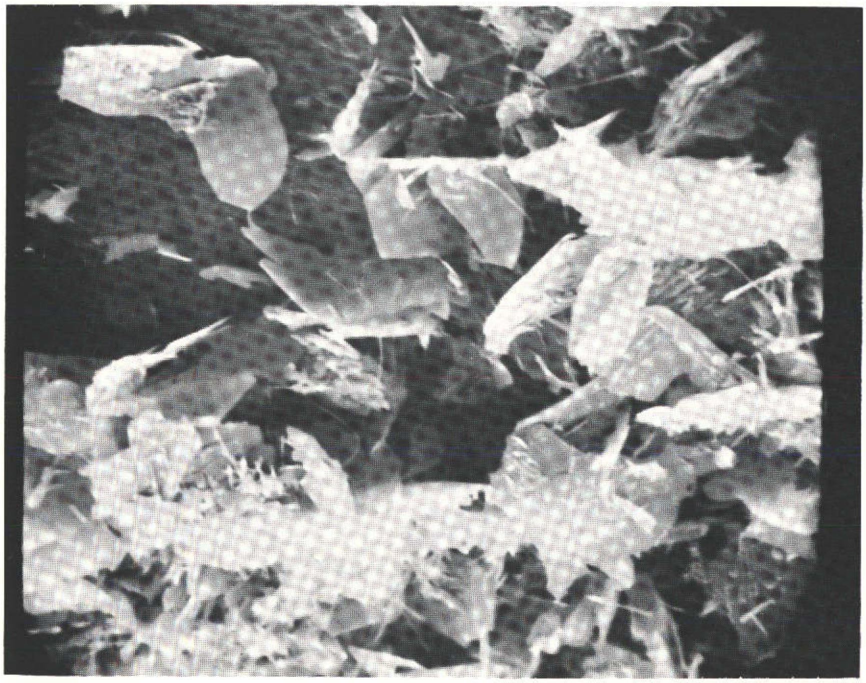


FIG. 10 BORON GROWTH ON TANTALUM - 704-713°C **2150X**

a electron micrograph of the "powder" material formed during the deposition of boron onto a tantalum substrate held at 704 - 713° C. in Run 3177-26. The magnification of Figure 9 is 950 X, while the magnification of Figure 10 is 2150 X. The "powder" appeared to be made up of thin flakes of irregular shape and some needles. Some of the flakes were curved but many had relatively large planar areas. This powder material was similar to that observed in NASW 2094--where it was thought to be tantalum diboride.

As considered earlier in this report, similar powders were formed on other substrates at similar temperatures. For instance, Figure 11 is an electron micrograph of the deposit formed on a copper substrate at 744 - 749° C. in Run 3177-27. The magnification is 5850 X. The similarities to the deposits formed at tantalum of 704 - 713° C. are apparent. An added feature shown in Figure 4 was evidence that some of the platelets tended to form hexagons.

The above photomicrographs indicated that boron deposits underwent a significant change in morphology at higher temperatures. The small areas of growth shown in Figure 7 indicated that the change could be initiated at temperatures as low as 602 - 621° C. on a tantalum substrate. It should be noted, however, that while the average temperature of the substrate was held in the range 602 to 621° C. for the run, it is possible that the regions of growth were initiated by small spits or droplets of boron from the melt. These may have raised the temperature of the local regions considerably in excess of 621° C. The changeover to powder formation was extensive on toth tantalum and copper substrates at about 700° C. As reported in the earlier part of this report, "powder" formation also occurred on an alumina rod substrate held at 704 - 713° C. in Run 3177-26.

The samples used to obtain the following series of electron micrographs used both quartz and sapphire as the substrate materials. These substrates

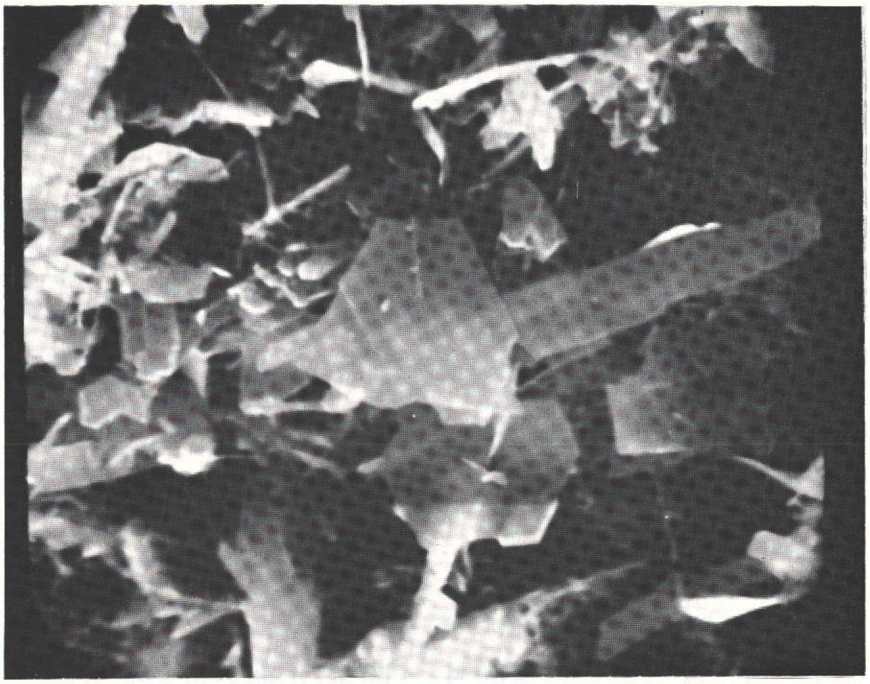


FIG. 11 BORON ON COPPER - 744-749 °C **5850X**

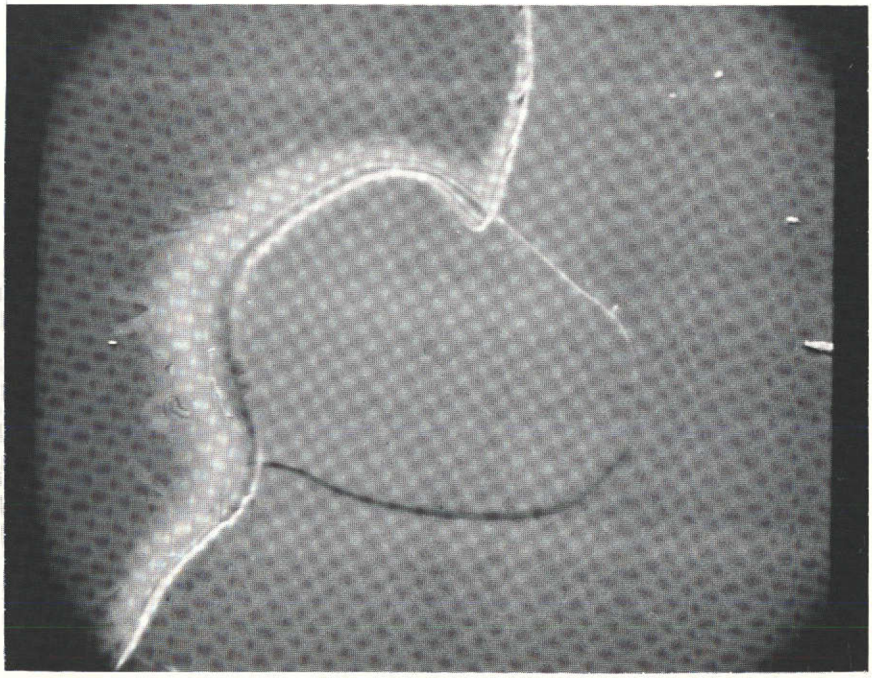


FIG. 12 BORON ON SAPPHIRE - 613-626 °C **230X**

were commercially available as highly polished, optically flat discs and plates. The sapphire had the added advantage of having a coefficient of thermal expansion close to that of boron.

Figure 12 is a scanning electron micrograph of boron deposited on sapphire at 613 - 626° C. in Run 3177-32. The magnification is 230 X. The photographed areas may be divided into three sections. The center "island" area is boron which appears to be raised above similar material which extends around a part of the "island". In the remaining area the boron had flaked off to leave the sapphire surface. When this occurred there was some marring of the sapphire. The curious type of fracture and the nature of the raised island area was peculiar to the sapphire substrate. Figures 13 and 14 are also electron micrographs of the boron deposits formed on the sapphire substrate at 613 - 626° C. Figure 13 shows the nature of the intersection of two crack zones at a magnification of 1215 X. Figure 14 shows the same intersection in more detail at a magnification of 6200 X. Extensive examination of these and similar micrographs did not provide satisfactory explanations for some of the details photographed. It did appear, however, that the boron deposited on polished sapphire at 613 - 626° C. was under compression with respect to the substrate. When a crack formed in the boron there appeared to be partial release of the boron from the substrate and the vertical displacement in Figure 14 may have resulted from a motion of one layer of the boron with respect to another. The raised regions may have formed during the deposition and may then have been overcoated with boron. The striations may have formed during the latter period. The curvature of the material on the upper parts of the crack, however, remain unexplained.

The fact that the boron deposit was under biaxial compression is shown more clearly in Figure 15. This is a scanning electron micrograph of boron

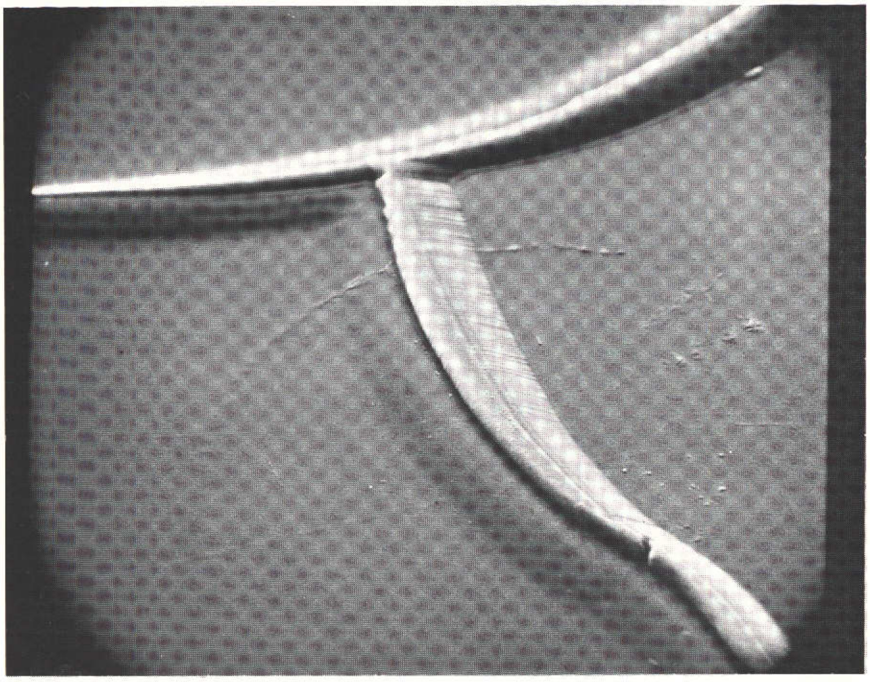


FIG. 13 BORON ON SAPPHIRE - 613-626°C **1215X**

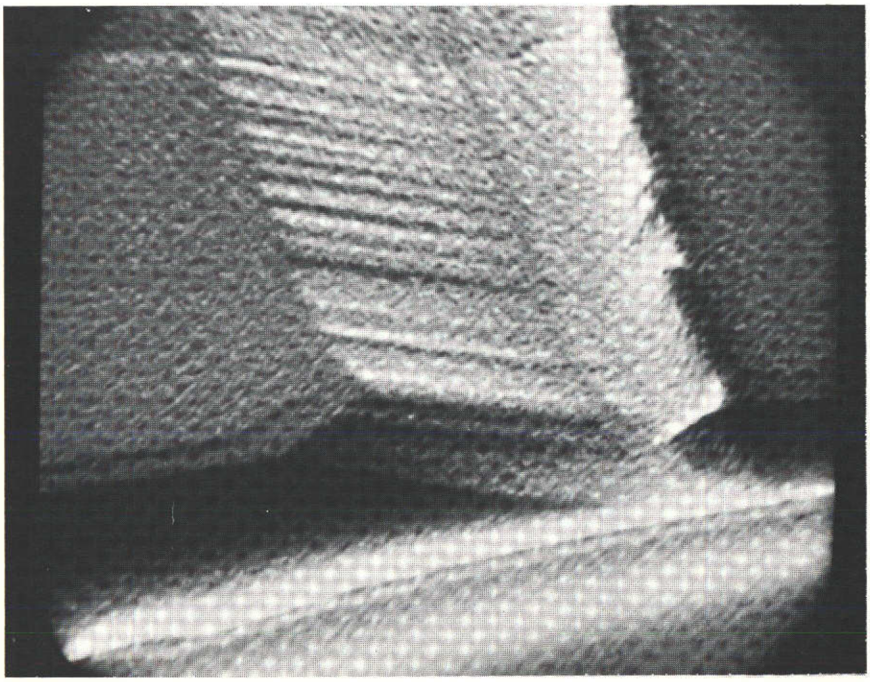


FIG. 14 CRACK ZONE IN BORON **6000X**

deposited on sapphire at 626 - 642° C. in Run 3177-34--about 20° C. higher than used to prepare the samples just considered. When released from the sapphire, the boron broke into convex sections (concave to the substrate). The release was energetic and rapid. The edges of the cracks were sharp and typical of brittle fracture. In these aspects they appeared different from the "cracks" shown in Figures 13, 14 and 15.

Figure 16 is an electron micrograph of boron deposited on a quartz substrate at 744 - 749° C. in Run 3177-27. The quartz was initially highly polished but for this experiment several scratches were made in the surface with a diamond scribe. The micrograph shows the intersection of two scratches after coating. The magnification is 237 X. Where the quartz was not scratched, the coating was black, shiny and mirror-like. However, in parts of the scratched regions, irregular growth was initiated. One area is shown in more detail in Figure 17 where the magnification is 2325 X. The structure was similar to that produced on tantalum, copper and the alumina rod. The above experiments indicated that irregular boron growth was promoted by sharp discontinuities in the surface of the substrate. Conversely, a necessary requirement for the formation of strong boron films would be substrates which were sufficiently smooth to preclude the formation of irregular growths of boron powder and crystals.

Some other types of defects which obviously affect the strength of boron films are shown in the remaining micrographs. Figure 18 is a micrograph of a defect formed during the deposition of boron on a polished silica substrate at 400 - 450° C. in Run 3177-36. The magnification is 2120 X. A droplet of boron impacted the boron deposit--probably toward or at the end of the deposition process. Smaller droplets were scattered in a circular pattern away from the main droplet. The "droplet" defect initiated the crack also shown in Figure 18.

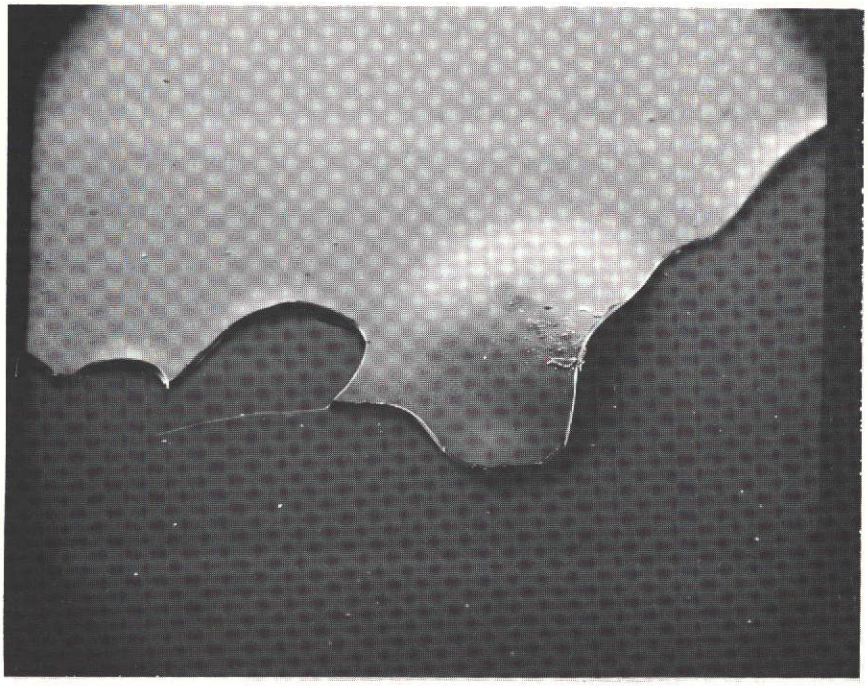


FIG. 15 BORON ON SAPPHIRE - 626 - 642°C **62X**

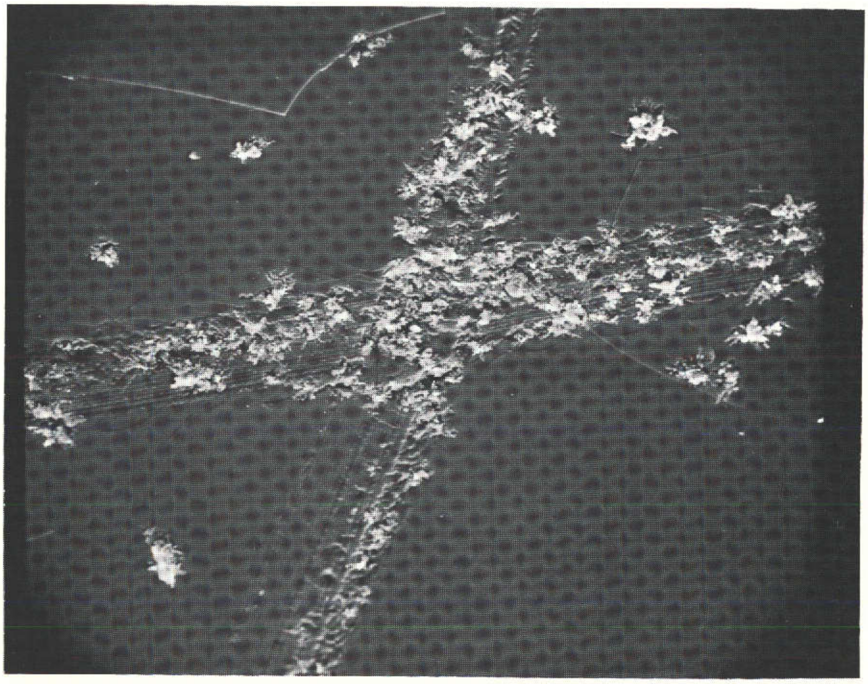


FIG. 16 BORON ON QUARTZ - 744 - 749°C **237X**

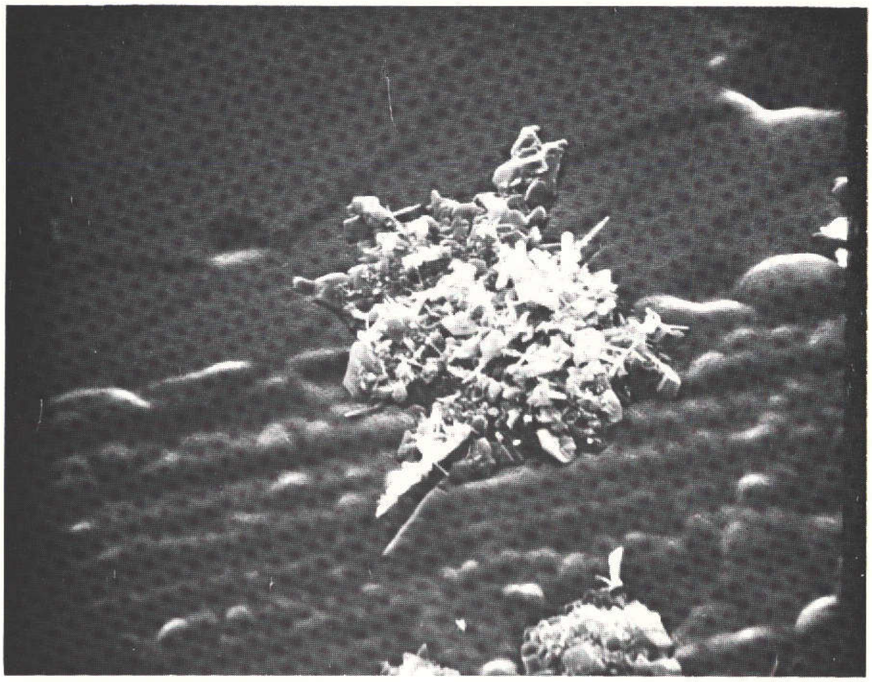


FIG. 17 BORON GROWTH ON SCRATCHES **2325X**

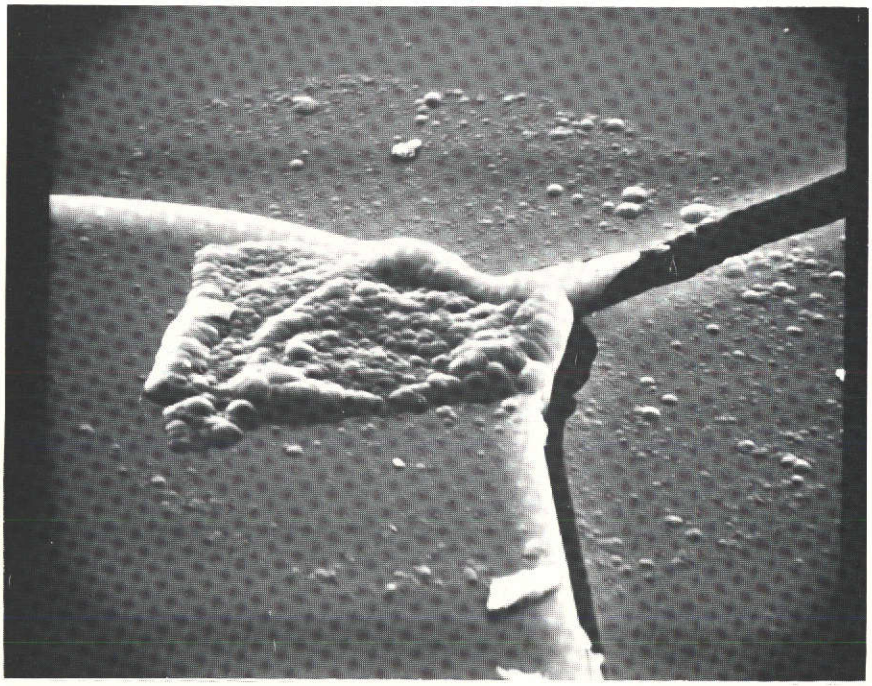


FIG. 18 DEFECT IN BORON FILM **2120X**

Similarly, Figure 19 shows a droplet which impacted another part of the boron surface during Run 3177-36. The magnification is 11,750 X.

Figure 20 shows a hole which was punched through a boron deposit at a time when the deposit was about 80-90% of its final thickness. This occurred in Run 3177-37 at 508 - 539° C. using a polished quartz substrate. The magnification of the photomicrograph is 860 X. This defect subsequently indicated the crack shown in Figure 20.

These types of defects were similar to those photographed in the earlier work under NASW 2094. The results confirmed that very small droplets of boron from the melt impact on the deposit with sufficient energy to produce defects in the deposit. Some of the droplets impinge as liquid, splatter and adhere to the deposit. It is possible that other droplets solidify before impact and do not adhere to the deposit. However, both droplet forms physically damage the surface of the deposit and cause defects, which undoubtedly reduce the strength of the films.

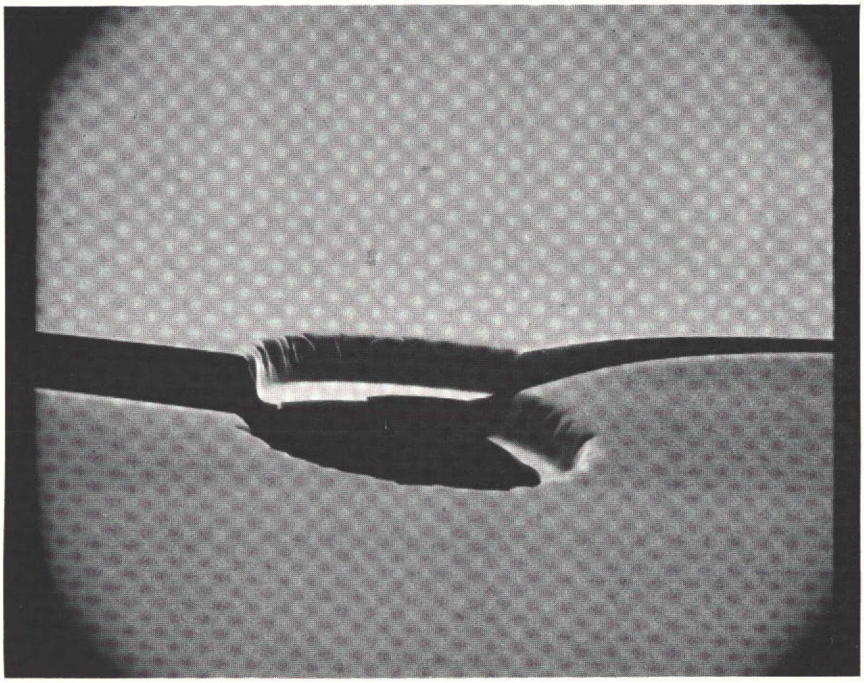


FIG. 19 HOLE IN BORON FILM **860X**

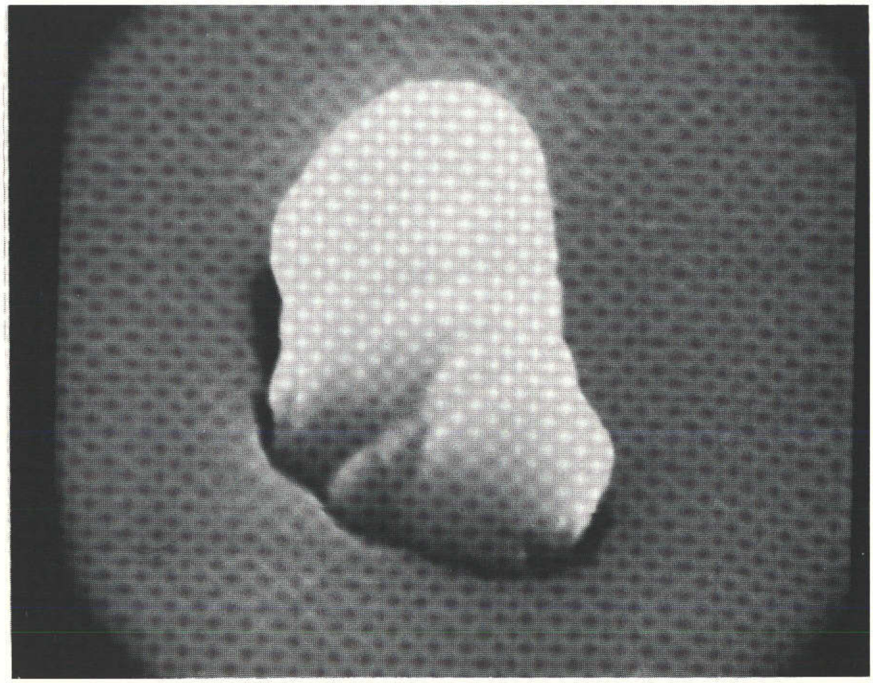


FIG. 20 INCLUSION IN BORON FILM **11,750X**

7. CONCLUSIONS

In the course of this program, boron was evaporated in vacuum by means of an electron beam. The boron vapor was condensed onto a selected series of substrates held at temperatures varying from ambient to approximately 750° C.

The properties of the boron deposits were significantly affected by substrate temperature, substrate composition and substrate morphology. The main results were:

7.1 Three distinct forms of boron were deposited. At temperatures below about 600° C., the boron deposit was "amorphous" to X-ray with calculated crystallite sizes of about 25 A°. If the substrate were highly polished, this boron was black and mirror-like. If, in addition, the coefficient of thermal expansion of the substrate were close to that of boron, the boron deposit was also continuous and uncracked.

Although the transition temperature was not sharply defined, two other forms of boron were produced at substrate temperatures in excess of 600° C. With highly polished quartz and sapphire substrates, transparent, orange-colored, continuous films of boron were produced. The films were highly stressed and changed to curved opaque black flakes when removed from the substrates.

When boron was deposited on scratched quartz, rough alumina rod, boron carbide, tantalum foil and copper, a finely divided gray powder deposit of boron was often formed at temperatures in excess of 600° C. Microscopic examination of the powder showed it to be made up of multiple platelets growing at different angles to one another. This form of boron did not reproduce to the morphology of the substrate. The platelets were more likely to grow from edges and at surface asperities on the substrate.

7.2 Measurements were made of the densities of flakes of boron after removal from the substrate. The measured values varied after the range from 2.200 to 2.357 g/cc. The lowest density material was formed on polyimide film at an average temperature of 140° C. The highest density material was formed on copper at 525° C.

Although there was considerable scatter in the data, the density of the boron deposit appeared to increase with temperature for both polyimide and copper substrates up to about 525° C.

A substrate temperature of at least 400° C. appeared to be necessary to have the density of the boron deposit approach that of the boron filaments (2.35 g/cc) made at about 1200° C.

The measured densities of deposits formed at temperatures in excess of 600° C. were less than 2.30 g/cc--significantly below the maximum of 2.357 g/cc. It is possible that density changes occurred when the highly stressed deposits were removed from the substrate.

7.3 X-ray diffraction studies of boron filaments made by chemical vapor deposition onto tungsten at about 1200° C.

showed the tungsten to be present mainly as WB_4 in the hexagonal phase. The boron was mainly amorphous, but peaks for rhombohedral and tetragonal boron were also present.

X-ray diffraction patterns were also obtained for boron deposited on tantalum, copper, quartz, sapphire and polyimide substrates by physical vapor deposition. For both the tantalum and copper substrates, the deposits were mainly amorphous boron, but the number of diffraction "peaks" increased with substrate temperature over the range 105 - 500° C.

Boron deposited on a tantalum substrate at greater than 300° C. had boron crystallite sizes comparable to that of the boron filaments. At 613 - 626° C. the boron on tantalum indicated some tetragonal boron structure. Boron deposited on copper also showed an increase in the number of peaks with substrate temperature, but crystalline phases of boron were not identified. Boron deposited on copper at 749 - 774° C. was highly ordered with relatively large crystallites.

Boron deposited on quartz and polyimide film was "amorphous". Boron deposited on polished sapphire at 307 - 374° C. and 602 - 621° C. had peaks with diffraction angles coincident with rhombohedral boron.

7.4 Boron was vacuum deposited onto thin tantalum substrates through dogbone "masks" for tensile strength measurements. The strength of vacuum deposited boron was estimated from measurements of the proportional limit strain of the boron-tantalum composites. Multiple layers of boron and tantalum were vacuum deposited on tantalum substrates, but the vacuum deposited tantalum was hard, brittle and weak. Multiple layers of boron and titanium were also consecutively vacuum deposited onto tantalum substrates. In these cases the titanium was ductile and higher boron strengths were attained. The highest proportional limit strain measured was 0.39%. This would be equivalent to a boron strength of 234 KSI.

The boron strength was not found to be dependent on the thickness of the boron layers. However, possible relationships were probably overshadowed by defects in the deposits caused by substrate roughness and damage resulting from droplets of boron from the melt impacting the boron deposits.

7.5 In general, the results obtained in the program indicated that substrate temperature played a major role in controlling the density of the deposit, crystallite size and whether or not the deposit was an amorphous film, a crystalline powder or a highly stressed transparent film. Tantalum substrates tended to promote crystal growth, while copper and polyimide tended to suppress it.

Transparent boron was formed on quartz and sapphire.

7.6 The work suggested that the following conditions would be necessary for the development of high strength boron films:

Prevention of droplets from the melt impacting the deposit
Use of highly polished substrates
Substrate temperatures in the range of 400° C. to 600° C.

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