



### Third Quarterly Progress Report

## A STUDY OF LOW DENSITY, HIGH STRENGTH, AND HIGH MODULUS WHISKER FILAMENT AND LAMINAR COMPOSITES

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For the Period

February 5, 1966 to May 5, 1966

Contract NASW 1347

25 May 1966

REPRODUCED BY: **NTIS**  
U.S. Department of Commerce  
National Technical Information Service  
Springfield, Virginia 22161

GENERAL TECHNOLOGIES CORPORATION  
708 North West Street  
Alexandria, Virginia

|                   |   |                       |
|-------------------|---|-----------------------|
| FACILITY FORM 408 | N66-85333<br>(ACCESSION NUMBER)           | (THRU)                |
|                   | 22<br>(PAGES)                             | <i>None</i><br>(CODE) |
|                   | CR-76159<br>(NASA CR OR TMX OR AD NUMBER) | (CATEGORY)            |
|                   |   |                       |



## ABSTRACT

Concurrent progress on the investigation of whisker reinforced, filament reinforced and laminar composites has been accomplished. Aligned silicon carbide whisker reinforced nickel composites have been tested which yield strengths of 327,000 psi with a modulus of 44.6 million psi at only eight to ten volume percent loading. Tungsten filament reinforced composite properties have been compared with law of mixture predictions over a range from 0 to 52 volume percent filament. Compressive strength values of 457,000 psi for boron-magnesium composites at 69 volume percent loading have been measured. Deposition parameters for the fabrication of adherent Mo-TiB<sub>2</sub> laminar composites have been developed.



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## I. INTRODUCTION AND SUMMARY

The work being conducted at the General Technologies Corporation under Contract NASw-1347 involves exploratory investigations of three major types of composite materials; filament reinforced metal matrix composites, whisker reinforced metal matrix composites and multilaminar, metal-ceramic composites.

Tungsten filament reinforced nickel composites, as prepared by the molecular forming process, were chosen for preparation and examination over a range of volume percent loadings. Whisker alignment was selected as the major problem to be overcome in the development of high performance whisker composites. The technology of vapor deposition was to be applied to the fabrication of a multilaminar metal-ceramic composite for evaluation as deposited and as reconstituted in the form of a cermet. The combination molybdenum-titanium diboride was chosen for this investigation.

During the first two quarterly report periods apparatus for the conduct of the various portions of the program were constructed. The deposition parameters for the preparation of high quality tungsten filament reinforced nickel composites were determined, composites fabricated, and mechanical tests performed. The deposition parameters for the formation of titanium diboride and molybdenum layered structures were determined. A number of techniques for the accomplishment of whisker alignment were examined and a simple technique was developed which yielded a highly aligned whisker yarn.

Accomplishments during the current reporting period include the completion of additional filament reinforced composite data, the improvement of interlaminar adhesion in the molybdenum-titanium diboride system, the development a metal

infiltration technique for the aligned whisker yarns and the generation of mechanical property data on infiltrated whisker yarn which indicates that a significant step toward the full utilization of whisker strength has been made. A strength increase of more than 200% over the matrix properties has been accomplished. Compressive strength values approaching one half million psi have been measured in the boron-magnesium system.

## II. LAMINAR COMPOSITE STUDIES

During this report period effort on laminar composites was centered on developing coherent deposits in laminar form. The system under study is molybdenum-titanium diboride, a system which has yielded good composite properties in the filament form. This system was selected for study in the laminar form because of the interest of NASA in molybdenum as a structural material and because titanium-diboride has a close thermal expansion match with molybdenum over the temperature range utilized in the vapor deposition process.

The objectives set for this phase of the program are:

1. determination of the deposition conditions for accomplishing the individual deposits,
2. determination of the best substrate for the initial deposited layer and the means for releasing the laminar composite from the substrate,
3. determination of procedures for obtaining maximum adhesion between the individual layers of the composite,
4. deposition of bi-layer composites and
5. deposition of multiple layer composites and mechanical testing.

The accomplishments toward these objectives are detailed below.

The apparatus described in the previous report was used for the deposition studies conducted during this report period. Molybdenum hexafluoride was used for depositing molybdenum and a titanium tetrachloride-boron trichloride gas mixture was used for depositing titanium diboride.

Table I summarizes the experiments conducted during this report period.

Table I. Mo-TiB<sub>2</sub> Multilayered Composite Deposition Studies

| <u>Sample No.</u> | <u>Deposition Temperature</u><br>(°C) |           | <u>Substrate</u>           | <u>Comments</u>                    |
|-------------------|---------------------------------------|-----------|----------------------------|------------------------------------|
|                   | <u>TiB<sub>2</sub></u>                | <u>Mo</u> |                            |                                    |
| III-A-1           | 1020                                  | -         | Graphite                   | 1-2 mil coating, X-ray             |
| III-A-2           | 1000                                  | -         | Mo foil                    | Coating flaked off                 |
| III-A-3           | 1002                                  | -         | Mo foil                    | Coating flaked off                 |
| III-A-4           | 1010                                  | 660       | Etched Mo foil             | TiB <sub>2</sub> Flaked, Mo spotty |
| III-A-5           | 1075                                  | -         | Etched Mo foil             | TiB <sub>2</sub> good adhesion     |
| III-A-6           | 950                                   | 655       | Etched Mo foil             | Coatings flaked                    |
| III-A-7           | -                                     | 665       | Graphite                   | System leaked                      |
| III-A-8           | 970                                   | 700       | Etched Mo foil             | Adhesion between coating           |
| III-A-9           | 1050                                  | -         | Electropolished<br>Mo foil | Coating flaked                     |
| III-A-10          | 1050                                  | 850       | Graphite                   | Good coating                       |

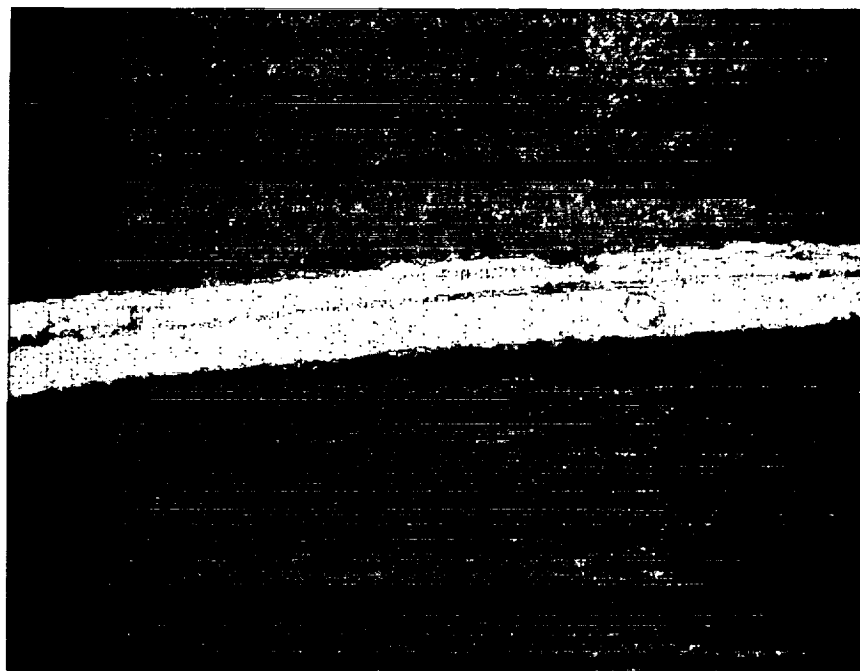
It was determined from these experiments that a temperature of 850°C gave good small grained deposits of molybdenum. A temperature between 1050 and 1100°C was required for the deposition of titanium diboride.

Considerable difficulty was experienced in developing a procedure which would give good adhesion between the deposit and the molybdenum foil substrate and between deposited layers. No problem was experienced in accomplishing adhesion to a graphite substrate. It was found that improved adhesion to molybdenum foil could be obtained if a thin layer of vapor deposited molybdenum was first deposited to the foil. It was also found that adhesion could be improved between molybdenum and a titanium diboride if the temperature of the sample was maintained while the deposition gases were being changed.

Figures 1 and 2 show two of the molybdenum-titanium diboride deposits obtained during this report period. Figure 1 shows molybdenum-titanium diboride deposited on molybdenum foil. While the layers are quite uniform delamination occurred along the interfaces. The sample was cooled down after the molybdenum was deposited. Figure 2 shows a similar composite on graphite. Good adhesion between the layers is apparent. However, the surface of the graphite causes a somewhat roughened deposit. The layers in this picture were taken at an oblique angle which exaggerates their thickness. The nickel overlayer was an electrodeposit to maintain the deposit edges in metallographic preparation.

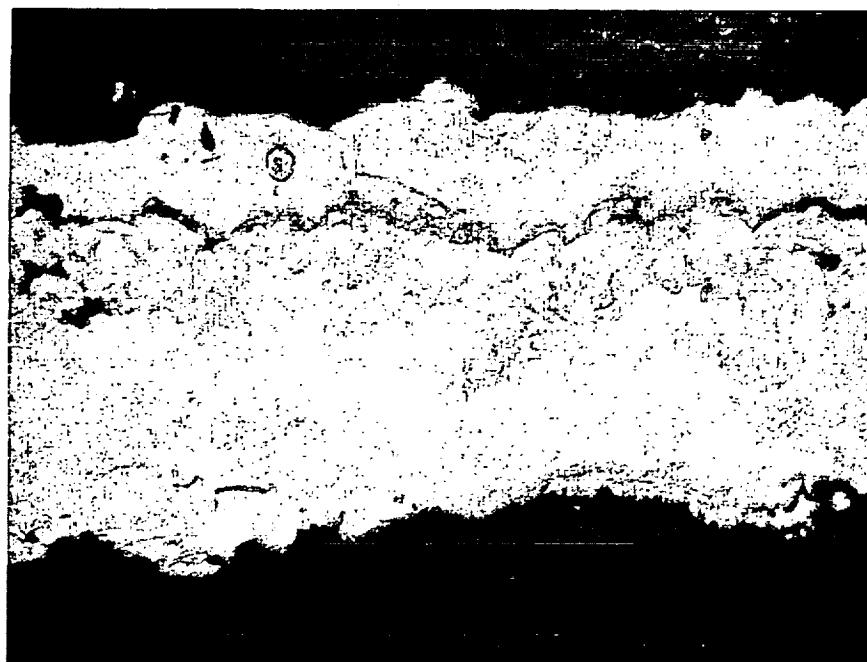
The experiments to combine the uniformity of the molybdenum foil deposits with the adhesion of the layers deposited on graphite are in progress and deposition rate information is being accumulated for control of the layer thicknesses.

During the next report period multilayer composites with various lamellae thicknesses will be deposited and tested.



— TiB<sub>2</sub>  
— Mo  
— Mo foil

Figure 1. Mo and TiB<sub>2</sub> Vapor Deposited onto a Molybdenum Foil Substrate, 400X



— Nickel  
— TiB<sub>2</sub>  
— Mo  
— Graphite

Figure 2. Mo and TiB<sub>2</sub> Vapor Deposited onto a Graphite Substrate, 200X



### III. WHISKER COMPOSITE STUDIES

The effort on the whisker composite phase of the program during this report period has concentrated on the infiltration of spun whisker yarns and the mechanical testing of infiltrated yarns. Single strands of nickel infiltrated whisker yarn have yielded strengths as high as  $327 \times 10^3$  psi.

The whisker yarn spinning technique was described in detail in the previous quarterly report. It consists of hand spinning a loose yarn of highly aligned whiskers from a mat of as-grown long fiber length silicon carbide whiskers, Thermokinetic Fibers Grade 5A. The whisker yarn prepared in this fashion was infiltrated by electro-deposition.

#### A. Infiltration of Aligned Whisker Yarns by Electrodeposition

The first attempts at infiltration by electrodeposition were conducted by supporting the whisker yarn vertically in a deposition bath on a metal C-frame. A horizontal support and a technique of mounting the whisker yarn on a stainless steel backing plate were also tried. These techniques suffered from a series of deficiencies:

1. The conductivity of the whisker yarn was dependent upon its thickness and the tightness of spinning.
2. The infiltration generally started at the whisker yarn ends and plated toward its center.
3. The plating rate was slow.

A technique of gradual immersion was more effective. The yarn was slowly dropped into the plating bath. The tip plated first and acted as a weight to straighten the yarn as it was immersed and coated. However this technique was relatively slow and yielded a tapered coating.

The best technique for electrolytic infiltration involved the spinning of a half mil nickel wire into the whisker yarn. A light weight could be connected to the nickel wire and electrical contact made to the other end. The ends of the spun whisker yarn were fixed to the wire with non-conductive lacquer and the balance of the wire was likewise coated to prevent plating except through the whisker yarn. This technique yields relatively good quality specimen for mechanical test as shown in Figure 3. The specimen is uniform on a gross scale but does have an undulated surface. The wire specimen is further smoothed with emery paper prior to mechanical testing.

#### B. Mechanical Testing of Infiltrated Whisker Yarns

The infiltrated whisker yarns are tested in the Tinius Olsen Electromatic tensile testing machine. The wire specimen is mounted on metal tabs with epoxy cement. The tabs are pin mounted in the tensile machine grip and tested. On specimens with a highly uniform cross section over a one inch gauge length, an extensometer is attached to the specimen and a modulus is determined from the load-elongation curve.

Because of the unconventional nature of the wire specimen fracture cross-section measurements were made on each specimen. The cross sectional measurement utilized for flexure and tensile modulus determinations was the average micrometer reading for six measurements along the gauge length. This is a most conservative cross sectional measurement and the data presented are substantial underestimates of the composite modulus.

The mechanical test results for the specimens tested to date are presented in Table II.

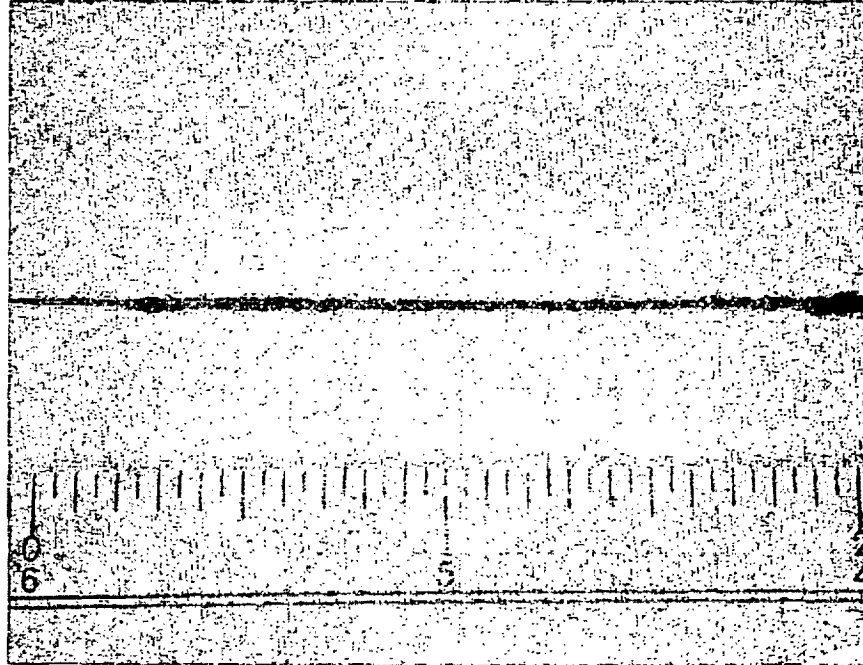


Figure 3. An Axially Aligned Whisker Yarn Infiltrated with Nickel by Electrodeposition

Table II. Mechanical Properties of Nickel Infiltrated Whisker Yarn Specimens

| <u>Specimen No.</u> | <u>Tensile Strength<br/>(10<sup>3</sup> psi)</u> | <u>Modulus<br/>(10<sup>6</sup> psi)</u> |
|---------------------|--|---|
| II-E10              | 85.1   | 30.8                                    |
| II-E11              | 183  | -                                       |
| II-E12              | 92.3   | -                                       |
| II-E13              | > 215  | -                                       |
| II-E20              | 170  | 44.0                                    |
| II-E21              | 169  | -                                       |
| II-E22              | 226  | -                                       |
| II-E23              | 226  | -                                       |
| II-E24              | > 185  | -                                       |
| 9 A 1               | 90.5   | -                                       |
| 9 A 2               | > 240  | -                                       |
| 9 A 3               | 327  | -                                       |
| 10 A 1              | 144  | -                                       |
| 10 A 2              | 184  | -                                       |

The values obtained for both tensile strength and modulus are remarkable for the first products of this composite fabrication scheme. Perfect uniformity in the spun yarn is not a characteristic of the spinning process in its current state of development. The variations in whisker density along the spun yarn dictates that the infiltrated wire will fail at the cross section containing the minimum volume percent whiskers. The low strength values represent the first test on a single yarn. Subsequent retests eliminate the weak points and yield the higher values. The volume percent loading cannot be derived from inspection of the fracture cross section. The specimen must be mounted and polished back to yield a metallographic surface for evaluation. The detailed work required to accurately assess the generated data is time consuming but every effort is being made to extract the maximum amount of information from each prepared whisker reinforced specimen. Fractured pieces of whisker wires are being extracted from mounting material and saved for reconstitution into a bulk specimen by hot pressure bonding.

The detailed analysis of the whisker data is only possible for two of the specimens tested thus far. Specimens IIE11 and IIE22 were photographed in cross section adjacent to their fracture surfaces and volume percent loadings of whiskers calculated. These specimens were calculated to have approximately 8 and 10 v/o whiskers respectively. Subtracting the contribution of the electrodeposited nickel matrix from the measured strength, the whiskers contributed 83,000 and 126,000 psi respectively. The calculated average strength of the whiskers in the composite with those volume percent loadings were 1.0 million and 1.2 million psi respectively.

It is impossible to assess the efficiency of whisker utilization since a statistical testing program on the whisker population from which the whisker yarns were spun,

would be required to arrive at an average whisker strength. The progress in this stage of the composite development program will be measured by the gross strength values on the wire specimens (a measure of the combined effect of density of loading and whisker utilization efficiency) and by the average strength attributed to the whiskers in composite. Considerable effort is being devoted to the development of a rapid statistically valid means of accomplishing the quantitative metallography for the determination of volume percent whiskers.

Figure 4 is a typical infiltrated whisker yarn cross section at 200X. Figure 5 and 6 are photomicrographs at 1500X of the whisker reinforced portion of the cross section on two different specimens. There is a distinct difference in the average size of the whiskers spun into the yarn for these specimens. No comment can be made at this time as to the relative strengthening power of the different sized whiskers in composite form.

Future work will be directed toward the accomplishment of higher volume percent loadings by increasing the density of the spun yarn and reducing the amount of nickel overplating. An effort will be made to accumulate a sufficient number of pieces of aligned whisker wire to form by hot pressure bonding a gross composite for mechanical test. In such a structure the longitudinal inhomogeneities of the individual wires will be averaged out and more consistently high mechanical properties should be derived.

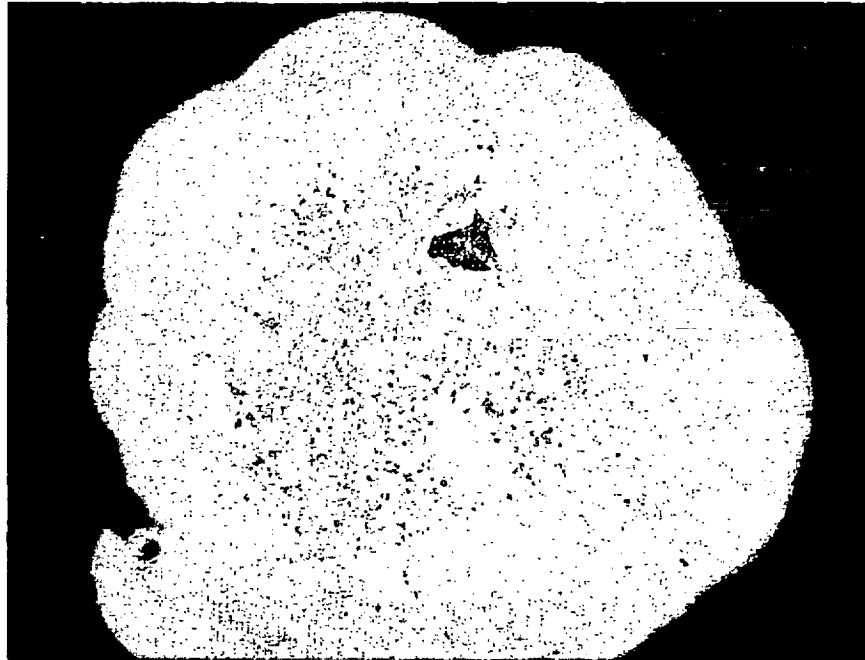


Figure 4. Crosssection of a Nickel Infiltrated Aligned Whisker Yarn, 200X

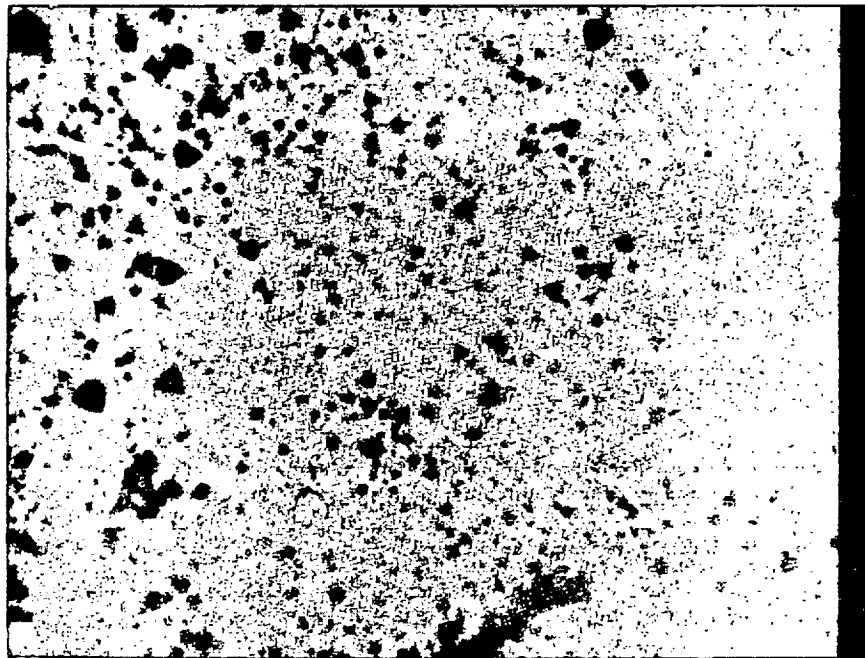


Figure 5. The Distribution of Whiskers in a Nickel Infiltrated SiC Whisker Yarn, 1500X



Figure 6. The Density of Whiskers in a Nickel Infiltrated Whisker Yarn Containing Relatively Large SiC Whiskers, 1500X



#### IV. FILAMENT COMPOSITE STUDIES

Tungsten filament reinforced nickel matrix composites fabricated by the molecular forming technique have been prepared over the volume percent filament range of 0 to 52%. The mechanical testing of uniaxial tensile specimens cut from continuous filament windings has been conducted and reinforcement behavior over the indicated range is tabulated in Table III. The results of the mechanical testing program are plotted on a tensile strength and modulus versus volume percent filament basis in Figures 7 and 8 respectively. The law of mixtures line for each property is indicated in the figures. Measured values scatter about the law of mixtures lines. Values at the higher volume percent loadings tend to fall below the line. At the lower volume percent loadings a significant number of results exceed law of mixtures values. At the higher volume percent loadings only the best specimens reach law of mixtures predictions.

Some effort was devoted to the measurement of compressive strength of continuous tungsten filament reinforced nickel composites. A special flat faced mandrel was utilized for winding the compression specimen and thick specimens were fabricated. The resultant specimens were placed in a fixture designed to prevent buckling in the compressive test. The ends of the sheet specimen protruded from the fixture. In each test performed on these specimens failure occurred by buckling of the portion of the specimen protruding from the supporting fixture. Efforts to fabricate helically wound filament reinforced composites were terminated because sufficiently high quality samples could not be prepared on the modest winding equipment currently available.

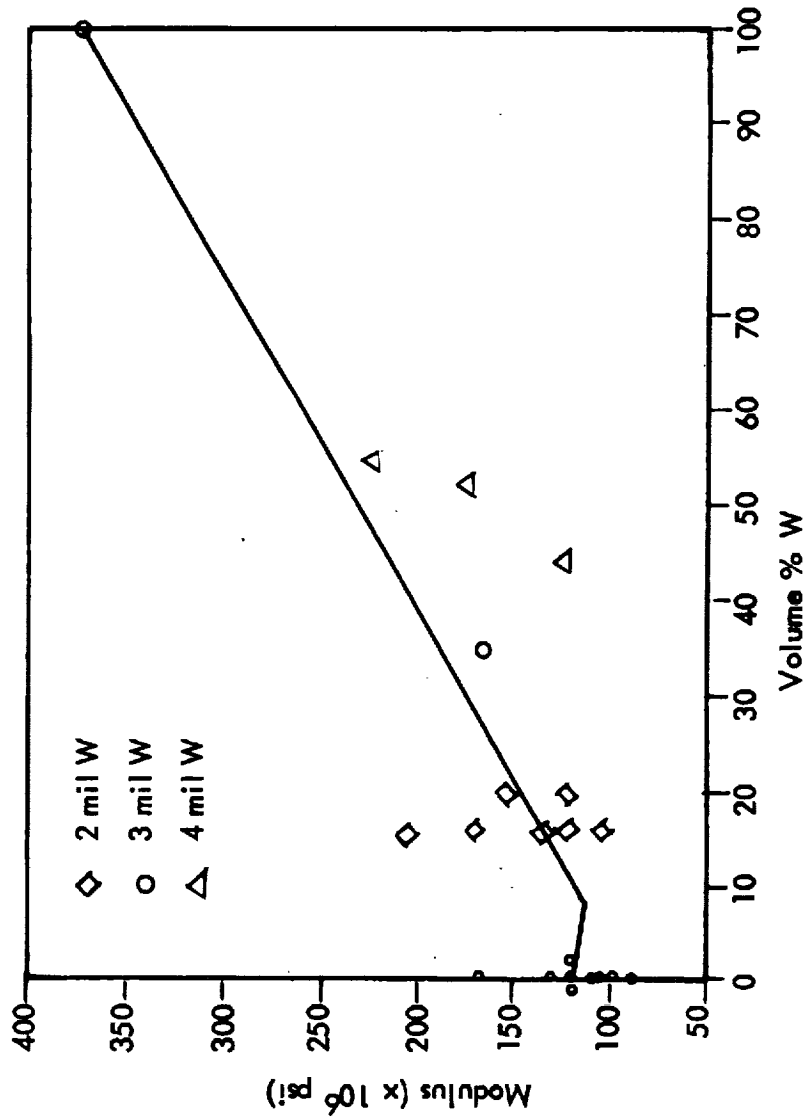


Figure 7. Tensile Strength versus Volume Percent Filament for Tungsten Wire Reinforced Nickel Composites

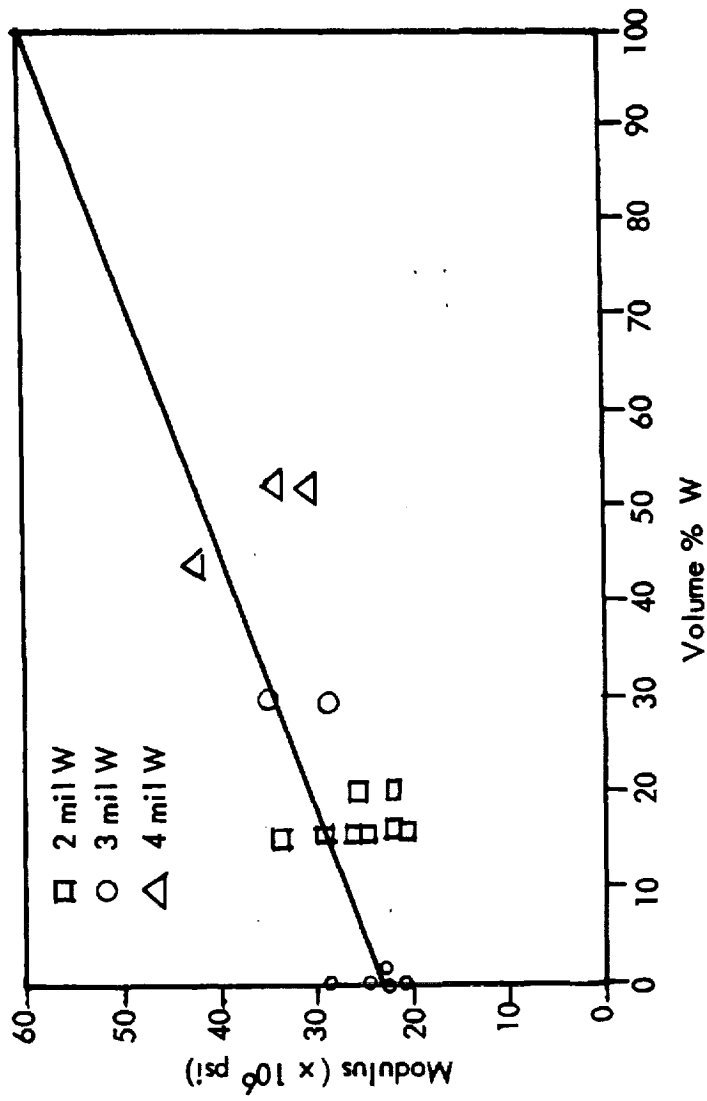


Figure 8. Tensile Modulus versus Volume Percent Filament for Tungsten Wire Reinforced Nickel Composites

Table III. Tensile Properties of Tungsten Filament Reinforced Nickel Matrix Composites

| <u>Volume %<br/>Filament</u> | <u>Tensile Strength<br/>(10<sup>3</sup> psi)</u> | <u>Modulus<br/>(10<sup>6</sup> psi)</u> |
|------------------------------|--|---|
| 0                            | 87.4   | -                                       |
| 0                            | 101.9  | -                                       |
| 0                            | 106.0  | 20.9                                    |
| 0                            | 109.6  | -                                       |
| 0                            | 119.0  | 28.8                                    |
| 0                            | 120.0  | 23.2                                    |
| 0                            | 120.6  | 24.8                                    |
| 0                            | 130.0  | 23.8                                    |
| 0                            | 168.0  | 23.8                                    |
| 15.5                         | 203.0  | 33.6                                    |
| 16                           | 105.0  | 20.5                                    |
| 16                           | 124.0  | 24.9                                    |
| 16                           | 127.0  | 21.4                                    |
| 16                           | 132.0  | 25.8                                    |
| 16                           | 170.0  | 29.2                                    |
| 20                           | 121.0  | 21.3                                    |
| 20                           | 152.0  | 25.4                                    |
| 29.8                         | -  | 28.4                                    |
| 29.8                         | -  | 34.9                                    |
| 34.5                         | 166.0  | -                                       |
| 44.2                         | 122.0  | 42.1                                    |
| 52                           | 175.0  | 30.1                                    |
| 52.5                         | 221.0  | 33.8                                    |

Because of the indicated NASA interest in compressive properties of filament reinforced composites additional effort was devoted to the generation of test specimens in the form of short cylinders or rectangular columns. Two fabrication techniques were developed for two different kinds of composites. Magnesium boron filament composites were prepared by the hot pressing of layers of electrolytically deposited aluminum-boron tapes.

The aluminum-boron tapes were prepared by winding a two inch width of continuous filament on a mandrel within an aluminum electroplating bath while concurrently electrodepositing the aluminum. The electroplating bath is an ethereal solution of lithium aluminum hydride and aluminum chloride. The generated tape containing well spaced boron filaments was cut into segments and charged in a hot press die. The multilayered array was pressed at 500°C for ten minutes at a pressure of 200,000 psi. The resulting specimens have been cut into various length columnar specimens and the ends are to be diamond ground flat and parallel. The first such specimens are currently being prepared for mechanical testing.

The magnesium-boron system has been observed to be the only metal-boron system which can be fabricated by liquid metal infiltration without significant degradation of filament properties. Thus the formation of high quality composite specimens by liquid metal infiltration is possible in this system. Magnesium-boron composites were successfully prepared by conventional vacuum infiltration techniques. Boron filaments were packed in a tube and magnesium drawn into the preheated array by vacuum.

The first magnesium-boron specimen has been machined and ground into a cylindrical compression specimen. The specimen was .669" in length and .138" in

diameter. It was tested between the hardened steel faces of a compression fixture in the Tinius Olsen Testing Machine. The specimen failed in compression at  $457 \times 10^3$  psi. The failure was by crushing of the one end of the specimen which canted the specimen and caused it to fly out of the compression cage. There was only superficial delamination at the outside surface of the specimen on one side. The fractured specimen is pictured in Figure 9. The modulus value was measured at  $23 \times 10^6$  psi by crosshead motion but this value includes the indentation of both faces of the hardened steel compression fixture by the boron reinforced specimen. Tungsten carbide flats are being procured to permit the accurate measurement of compressive modulus.

The compressive strength registered by this specimen is most remarkable. The specimen contained 69 volume percent filament. The specimen did not delaminate indicating that the matrix is well bonded to the filament and is strong enough to accommodate the developed transverse stresses.

The utility of magnesium and magnesium alloys as structural materials is substantially restricted by its poor corrosion resistance. However space environments do not present such corrosion problems and serious consideration should be given to the utility of hot pressed boron reinforced magnesium panels for high modulus high strength applications in both tension and compression.

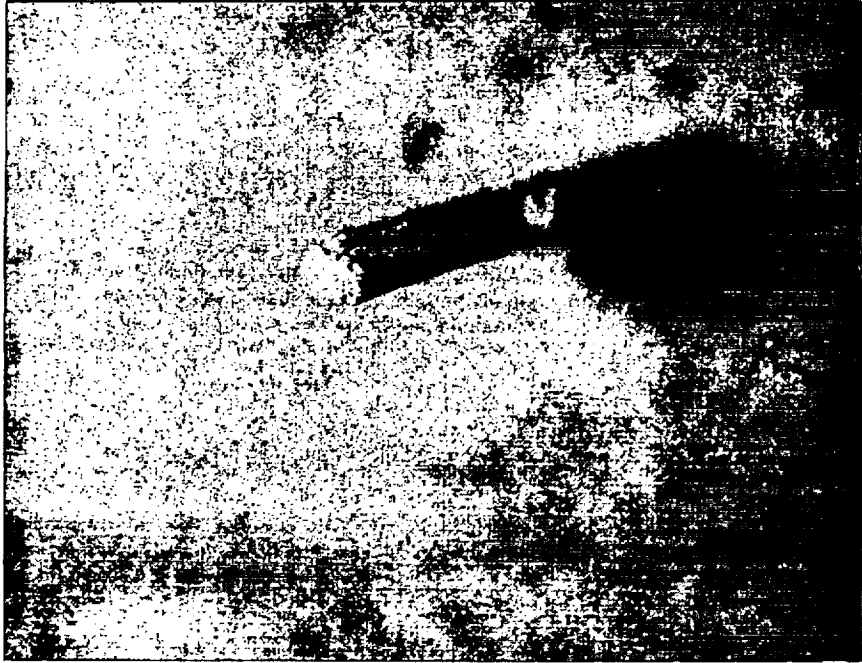


Figure 9. Compression Tested Boron-Magnesium Composite Specimen





## V. FUTURE WORK

Aligned whisker composites will continue to be fabricated and tested. Accurate quantitative metallographic techniques will be applied to volume percent whisker determinations. Aligned whisker wires will be hot pressed into a gross aligned whisker specimen. Compressive properties of magnesium-boron and aluminum-boron composites will be determined at various volume percent loadings. Multilaminar composite specimens will be prepared for mechanical testing.

