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FINAL REPORT

NEW STRUCTURAL MATERIALS

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SUMMARY

Twenty-four experiments were performed in which reinforcing fibers were used in combination with SHS (Self-Heating Synthesis) reactants in an attempt to prepare reinforced ceramic bodies by this process. Some fibers, especially those made of tungsten, silicon carbide, and zirconia, survived the reaction conditions. However, the ceramic bodies displayed cracks and voids. Examination by SEM of cross-sections of the reacted parts made with tungsten fibers disclosed the presence of "whiskers" of a general composition TiW B_x.

High frequency transmission data of a TiB_2 loaded polyimide molded part were obtained.

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ABSTRACT

New high temperature structures need to be developed that are based on intermetallic materials and ceramic composites. High density borides and carbides previously have been synthesized by self-propagating high temperature synthesis using reaction pressing techniques in the absence of external heating. Based on this technique, new materials (dense reinforced structures) were synthesized using titanium boride as a primary matrix, with second phase brittle components such as carbon particles, carbon cloths, silicon and silicon carbide filaments, as well as ductile second phase additions, such as several forms of nickel or chromium. The effects of the additions on the mechanical and physical properties of those materials were examined as a function of temperature and composition. The interaction of matrix/reinforcement during the exothermic formation was studied. A new filler material also was used with high temperature resin to demonstrate composites with higher temperature capabilities and low observable properties. The resulting materials were expected to have improved toughness, oxidation resistance, and high temperature survivability.

INTRODUCTION

Refractory fibers have been used as reinforcements in combination with metal alloys to form reinforced composite bodies (Ref. 1). The use of similar fibers as reinforcements in ceramic bodies made by the SHS (Self Heating Synthesis) process has been investigated in this program. In particular, the formation of TiB_2 by the following reaction:

$$Ti\ (s) + 2B\ (s) \longrightarrow TiB_2\ (s) + 22\ kcal/mol\ (or\ 1.2\ kcal/g)$$

has been used to form ceramic parts. The adiabatic temperature of the reaction is about 3600°K, which exceeds the melting point of TiB_2 (3193°K). This means that the TiB_2 goes through a liquid phase during and/or after the reaction. Any reinforcing fillers, in order to retain their shape and perform a useful function,

must be able to withstand the elevated temperature of the reaction, and the extremely reactive species present during the liquid phase.

TECHNICAL DISCUSSION

Materials that have a sufficiently elevated melting point to be useable in the SHS reaction previously discussed, and in addition, can be made into fibrous reinforcements, are extremely limited in number, as can be seen in Figure one (Ref. 2). In addition, these materials must be able to withstand the chemical reactivity of the SHS materials during the liquid phase portion of the reaction. Ideally, a reinforcement would retain its fibrous (or any other desired) shape while bonding strongly to the ceramic body.

From Figure One, a listing of suitably thermally stable materials can be made:

TABLE I. THERMALLY STABLE MATERIALS*

MATERIAL	MELTING POINT K°	(C°)
Hafnium Carbide	4160	(3887)
Tantalum Carbide (TaC)	4150	(3877)
Niobium Carbide	4023	(3750)
Carbon (Graphite)	3970	(3697)
Zirconium Carbide	3805	(3532)
Tungsten 3643	3643	(3370)
Tantalium Carbide (Ta_2C)	3573	(3300)
Hafnium Nitride	3523	(3250)
Rhenium	3440	(3167)
Thoria (ThO_2)	3423	(3140)
Zirconia (ZrO_2)	3273	(3000)
Titanium Diboride (TiB_2)	3193	(2920)
Silicon Carbide (SiC)**	2973	(2700)

*Having melting points greater than the melting point of TiB_2
**Included in the listing because of availability as a fiber (Nicalon®).

TABLE 2. CARBON/GRAPHITE FIBERS

MATERIAL	FILAMENT DIAMETER MICRONS	SPECIFIC GRAVITY	ULTIMATE TENSILE STRENGTH PSI	TENSILE MODULUS PSI	USE T°K (MAX.)
AS 1 (H)	8	1.80	280×10^3	33×10^6	3300
AS 2 (H)	8	1.80	400×10^3	33×10^6	
AS 4 (H)		1.80	550×10^3	34×10^6	
AS 6 (H)	5	1.83	600×10^3	35×10^6	
IM 6 (H)		1.73	635×10^3	40×10^6	
IM 7 (H)	5	1.78	635×10^3	41×10^6	
HMS4 (H)	8	1.80	360×10^3	49×10^6	
HMU (H)	8	1.84	400×10^3	55×10^6	
T50 (A)	6.5	1.81	350×10^3	57×10^6	
T300 (A)	7	1.76	500×10^3	33.5×10^6	
T500 (A)	7	1.79	575×10^3	35.5×10^6	
P25 (A)	11	1.90	200×10^3	23×10^6	
P55 (A)	10	2.0	275×10^3	55×10^6	
P75 (A)	10	2.08	300×10^3	75×10^6	
P100 (A)	10	2.15	325×10^3	105×10^6	
P120 (A)	10	2.18	325×10^3	120×10^6	
GY 70 (B)	8	2.05	400×10^3	70×10^6	

H - HERCULES

A - AMOCO PERFORMANCE PRODUCTS

B - BASF

It should be emphasized that Table I is by no means a complete listing of thermally stable materials, but concentrates on materials either available in the form of high aspect ratio reinforcements, or have the potential of being made in that form. Of all the materials listed, the most readily available in the form of fibers are those based on carbon. Table 2 lists some representative carbon/graphite fibers that are currently available commercially. Note that the modulus characteristics are directly related to the density of the fiber, and that the degree of crystalline orientation of the graphite structures in the fiber also increases as the density increases. While it is well known that carbon reacts with the SHS reaction mixture at elevated temperatures, two fibrous materials based on carbon, and one based on silicon carbide, were selected in the hope that a highly oriented, crystalline structure would survive reaction conditions. As a result, T300 (a medium modulus fiber) and GY70 (a high modulus fiber, were selected for investigation. A silicon carbide fiber (Nicalon) was also selected. All three of these materials were available in the form of woven fabrics. Other fibers that were investigated include tungsten (wire) Zirconia fiber, and steel (wire). Rhenium is also available as a wire or fiber, but, because of its high cost, was not investigated.

The capability of reinforcements to withstand SHS reaction conditions was investigated by incorporating fibers into a dry mix of SHS reactants and placing the resulting combination of materials in a steel die as shown in Figure 2. The die was insulated with alumina wool (not shown in the sketch). The experiment was performed by placing the die in a spring loaded hydraulic press as shown schematically in Figure 3,applying pressure, and igniting the pyrofuse electrically. The pyrofuse initiated the SHS reaction, and the springs kept pressure on the pistons as the reaction proceeded. THe reaction generates a great deal of heat, and the reactants liquefy, occupying less space and causing the pressure pistons to move closer together.

Experiments were performed by incorporating fibers into the reaction mix using a tumbler mixer. Fabrics were cut into small pieces before incorporation. Fibers, wires, and tows were cut into one inch lengths. Table 3 outlines the compositions used and the results obtained after pressing the materials previously described. The materials and processes developed during the performance of Contract No. DAAL04-87-C-0083 "Self Heating Synthesis of High Density TiB_2" were used whenever appropriate.

The experiments listed in Table 3 are identified by a code number and a sequence number. In the interests of brevity, sequence numbers will be referred to hereafter.

Experiment 1 used GY 70 fibers as a reinforcement. Even though only a small amount of fiber was added to the reaction mix (4% by weight), the reaction was so violent that much of the material was blown out of the die, and only small fragments of questionable composition were left. Density was low, and the pieces were porous.

For experiment 2, tungsten wire was used. The reaction materials were lost due to a poor fit in the die parts. Experiment 3 used Nicalon silicon carbide fiber. The reaction was violent, causing much loss of material. A few pieces of varied composition were examined, showing surprisingly high density. Experiment 4 was a repeat of experiment 3 with a more carefully packed die. Once again, there was excessive material loss during the reaction.

Experiments 5 and 6 used closer fitting plungers and there was very little loss of reactants. The products were cracked and broken into small pieces, but microscopic examination showed that the tungsten wires had survived the reaction intact.

Experiments 7 and 8 used silicon carbide fibers (Nicalon) as the reinforcement. Number 7 produced a cracked, porous part, while number 8 reacted so violently that all reactants were lost. Microscopic examination of number 7 was

unable to disclose any surviving fibers, indicating that they had reacted with the other materials.

Experiment 9 was an attempt to see if reducing the nickel content and adding some pre-reacted TiB_2 would control exotherm characteristics and reduce cracking. This approach was not successful, and a cracked, porous mass of relatively low density was the result.

Experiment 10 was another attempt to use silicon carbide fibers. A violent reaction, resulting in excessive material loss, took place. At this point, the decision was made to stop further attempts using silicon carbide and carbon fibers because of the difficulties with reactivity mentioned.

Experiments 11 and 12 used zirconia fibers. The product was cracked and porous, but microscopic examination showed that the fibers had survived the reaction.

Experiments 13 and 14 used tungsten wire of two different diameters. Solid parts with intact wires resulted in both cases, but cracks and porosity were present.

Experiment 15 used chromium powder as a modifier in place of nickel. Once again, a porous, cracked part resulted.

Experiments 16 and 18 used steel wire as a reinforcement. The melting point of the steel is too low to withstand the reaction temperature, and the wire melted. It did, however, act as a restraint and prevented the loss of reactants to a great extent. The parts thus made were cracked and broken, but the density was fairly high in the case of number 16.

Experiments 17, 19, and 20 used tungsten wire reinforcements. Number 19 did not fire completely, but numbers 17 and 20 produced parts that were able to be examined, even though cracks and porosity were present. Adding some pre-reacted TiB_2 (number 20) to the mix appeared to control the reaction and gave a higher density part, even though an intact piece was not made.

Experiment 21 was an attempt to increase the zirconia content from the previously used 5% to 10%. The mix failed to fire, probably because of dilution effects.

Experiment 22 used nichrome wires in the mix. These wires melted during the reaction, and a cracked, porous, low density part resulted.

Experiment 23 used zirconia fibers and a chromium modifier. Fibers survived intact, and a cracked, porous, low density part resulted.

Experiment 24 was an attempt to increase the chromium content of the mix so that improved toughness and (hopefully) fewer cracks would result. Unfortunately, the mix would not ignite, probably because of the dilution effect of the chromium.

At this point it was decided to halt experiments using the spring-loaded press because of poor results-cracked and porous parts, in particular. However, valuable information was obtained on the compatibility of various fibers and modifiers with the Ti2B reaction system. Specifically, carbon and silicon carbide fibers should not be used because of the reactivity of these materials, even in a highly crystalline form. Tungsten and zirconia wires and fibers survived quite well. Materials like steel and nichrome have melting points that are too low to be useful.

Because of the cracks and porosity of the parts produced, no mechanical properties could be obtained. Figure 4 is a cross section (2.2 x) of the part made in experiment 17. It is fairly typical of the products made. Note porosity and cracks, as well as the intact tungsten wires.

Figure 5 is a higher magnification (60X) photomicrograph of the part made in experiment 17 sharing a tungsten wire in a TiB_2 matrix. The irregular outline of the tungsten, showing attack by the hot reactants, is readily discernable. Figure 6 shows an area of the same part (at 2400X) in which whiskers grown during the reaction are seen. The whiskers have the composition $TiW\ B_x$.

TABLE 4. TRANSMISSION AND REFLECTANCE CHARACTERISTICS OF TiB_2/POLYIMIDE COMPOSITE

(20% TiB_2) SP.G. 1.93

FREQUENCY GHz	AIR TRANSMISSION db	SPECIMEN TRANSMISSION db	SPECIMEN REFLECTION db
3.8	- 9.4	-13.2	-16.8
3.9	- 9.2	-12.9	-16.4
4.0	- 8.4	-12.5	-15.8
4.1	- 8.5	-12.5	-15.9
4.2	- 9.1	-12.5	-16.3
4.3	-11.6	-12.8	-17.2
4.4	- 7.9	-13.2	-16.2
4.5	- 6.2	-10.3	-15.9
4.6	- 4.3	- 7.8	-16.3
4.7	- 3.7	- 7.2	-16.8
4.8	- 3.3	- 7.0	-14.2
4.9	- 3.3	- 7.5	-14.0
5.0	- 3.1	- 7.6	-14.1
5.1	- 2.6	- 7.1	-14.2
5.2	- 2.1	- 6.6	-14.5
5.3	- 1.8	- 6.6	-15.2
5.4	- 1.2	- 6.8	-16.3
5.5	- 0.5	- 7.4	-17.2
5.6	- 0.5	- 8.3	-16.8
5.7	- 0.5	- 8.1	-15.0
5.8	- 1.1	- 7.7	-11.2
5.9	+ 0.1	- 5.6	- 9.9
6.0	+ 0.6	- 5.6	-10.1
6.1	+ 0.5	- 4.4	- 9.5
6.2	- 2.3	- 6.9	-11.9
6.3	- 1.1	- 5.0	-11.0
6.4	- 0.9	- 5.8	-11.9
6.5	+ 0.5	- 2.3	-10.9
6.6	- 0.3	- 2.4	-17.2
6.7	- 1.8	- 2.9	-11.2
6.8	- 2.5	- 4.0	-11.4
6.9	- 6.3	- 6.1	-13.6
7.0	- 5.5	- 5.6	-14.7
7.1	- 3.4	- 5.3	-11.5
7.2	- 7.7	-13.7	-16.9
7.3	-12.6	-16.3	-14.6
7.4	-15.6	-10.9	-16.9
7.5	-16.8	-23.3	-15.8
7.6	-14.6	-18.7	-17.5

Figure 7 (260X) shows a bundle of SiC (Nicalon) fibers in a TiB_2 matrix. The fibers appear to have survived reaction conditions quite qell. At higher magnification (3200X) surface attacks on the fibers is evident, as shown in Figure 8. Figure 9 (3200X) shows plate-like structures formed in the TiB_2 where no SiC fibers are present.

Low observable composites based on a thermally stable organic resin , Thermid 600 moldable polyimide, were fabricated. Figure 10 is a DTA-TGA plot showing the thermal stability of the material. Molded parts were made by mechanically mixing powdered Thermid MC 600 with $\leq$ 325 mesh TiB_2, then comporessing the mix to shape in a steel die, followed by fusing at 180°C - 200°C for one hour. Composites containing 20%, 33%, and 50% TiB_2 were prepared. The 20% TiB_2 composite was mounted on a Sperry Directional Coupler (Model 605) equipped with a Sperry Isolator (Model D41C5). A Hewlett Packard SHF signal generator (Model 618B) was used to generate high frequency signals from 3.8 to 7.6 GHz, with readings taken at intervals of 0.1 GHz using a Hewlett Packard power meter (Model 431C). All readings were taken at room temperature (21°C). The data are presented in Table 4. When compared with the readings taken on air during the same test sequence, there was considerable variation in both transmission and reflectance characteristics of the composite, depending on frequency.

CONCLUSIONS

- Attempts to make reinforced composites with carbon fibers using SHS materials and processes were unsuccessful due to the reactivity of the fibers with the SHS reactants, resulting in violent reactions that, in most cases, blew the reactants out of the die. Fibers based on carbon are unsuitable for use in the SHS process.

- Tungsten and zirconia and silicon carbide fibers successfully withstood the reaction conditions generated by the SHS process. These fibers would be useful as reinforcements.

TABLE 3. COMPOSITE SHS PRESSINGS 3" DIAMETER DIE

SPECIMEN CODE (SEQUENCE NUMBER)	COMPOSITION	DENSITY (g/cc)	COMMENTS
102788-A (1)	1.15 Ti + 2B - 12% Ni GY 70 Fibers	3.6	Violent reaction - many small pieces
111888-A (2)	1.15 Ti + 2B - 12% Ni Tungsten Wire 0.025" diam.	-	High weight loss during reaction No recoverable pieces
111888B (3)	1.15 Ti + 2B + 12% Ni Nicalon Fibers	4.3	Violent reaction Many small pieces
112188-1 (4)	1.15 Ti + 2B - 12% Ni Tungsten Wire 0.125" diam.	-	Excessive material loss during reaction discarded
112388 (5)	1.15 Ti + 2B + 12% Ni Tungsten Wire 0.025" diam.	4.5	Well contained reaction cracked and porous
112388-1 (6)	"	3.86	" "
112388-2 (7)	1.15 Ti + 2B + 12% Ni Nicalon Fibers	3.68	Cracked and porous
112888 (8)	1.15 Ti + 2B + 12% Ni Nicalon Fibers	-	Violent - All reactants lost
112888-1 (9)	1.15 Ti + 2B + 6% Ni + 2% TiB_2	3.9	Cracked and porous
112988-1 (10)	1.15 Ti + 2B + 12% Ni Nicalon Fibers	-	Violent reaction - excessive material loss
120688 (11)	1.15 Ti + 2B + 12% Ni + 2% TiB_2 Zirconia Fibers	3.57	Well contained reaction cracked and porous

TABLE 3. COMPOSITE SHS PRESSINGS 3" DIAMETER DIE (Continued)

SPECIMEN CODE (SEQUENCE NUMBER)	COMPOSITION	DENSITY (g/cc)	COMMENTS
120788 (12)	1.15 Ti + 2B + 12% Ni + 2% TiB_2 Zirconia Fibers	3.78	Well contained reaction
120988-1 (13)	1.15 Ti + 2B + 12% Ni + 2% TiB_2 Tungsten Wire 0.050" diam.	3.7	Solid part Porous and cracked
121488-1 (14)	1.15 Ti + 2B + 10% Cr +2% TiB_2 Tungsten Wire 0.025" diam.	2.4	Extremely porous
121588-1 (15)	1.15 Ti + 2B + 10% Cr + 2% TiB_2 (No reinforcement)	-	Porous and cracked
121988-1 (16)	1.15 Ti + 2B + 10% Cr + 2% TiB_2 Steel Wire	4.24	Cracked
122088-1 (17)	1.15Ti + 2B + 10% Cr Tungsten Wire 0.050" diam.	3.9	Good material retention cracked and porous
122188-1 (18)	1.15 Ti + 2B + 12% Cr + 1% TiB_2 Steel Wire	3.3	" "
122388-1 (19)	1.15 Ti + 2B + 10% Cr + 1% TiB_2	-	Misfire - incompletely reacted
122888-1 (20)	1.15 Ti + 2B + 10% Cr + 1% TiB_2 Tungsten Wire 0.050"	4.4	Cracked and porous
123088-1 (21)	1.15 Ti + 2B + 10% Cr Zirconia Fibers (10%)	-	Unable to fire - excessive inert material (zirconia)

TABLE 3. COMPOSITE SHS PRESSINGS 3" DIAMETER DIE (Continued)

SPECIMEN CODE (SEQUENCE NUMBER)	COMPOSITION	DENSITY (g/cc)	COMMENTS
010389 (22)	1.15 Ti + 2B + 10% Cr Nichrome Wires	3.7	Cracked and porous
010489 (23)	1.15 Ti + 2B + 10% Cr Zirconia fibers (5%)	3.75	Cracked and porous
010689 (24)	1.15 Ti + 2B + 15% Cr No Fibers	-	Unable to fire - excessive inert material (chromium)

- Steel and nichrome wires are unsuitable because of low melting points.
- TiB_2/polyimide composites were prepared and tested at high frequencies.

Transmission and reflectance characteristics vary with frequency, showing energy absorption of the filled system.

RECOMMENDATIONS

More work is needed on the basic SHS reaction process in order to provide high density, intact parts. Once this has been accomplished, then the use of SiC, tungsten, and zirconia fibers as reinforcements at several loading levels can be evaluated. Polyimide resins loaded with borides at several levels of concentration can be easily prepared and should be evaluated at elevated temperature.

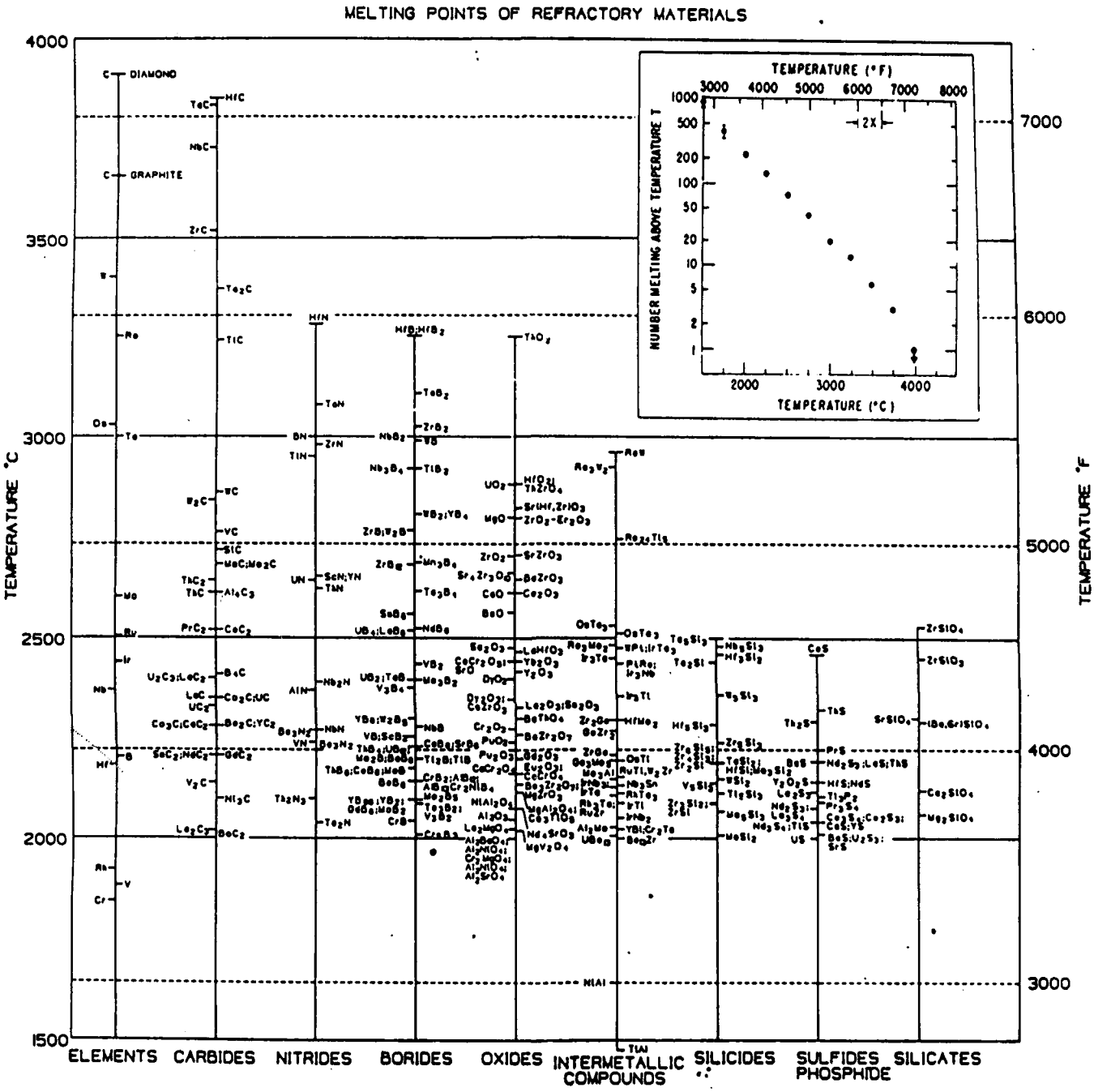


FIGURE 1. MELTING TEMPERATURES OF MATERIALS FOR WHICH T_m IS AT LEAST 2000°C. THE NUMBER OF MATERIALS THAT MELT ABOVE A GIVEN TEMPERATURE DROPS OFF EXPONENTIALLY WITH INCREASING TEMPERATURE, AS SHOWN IN THE INSERT.

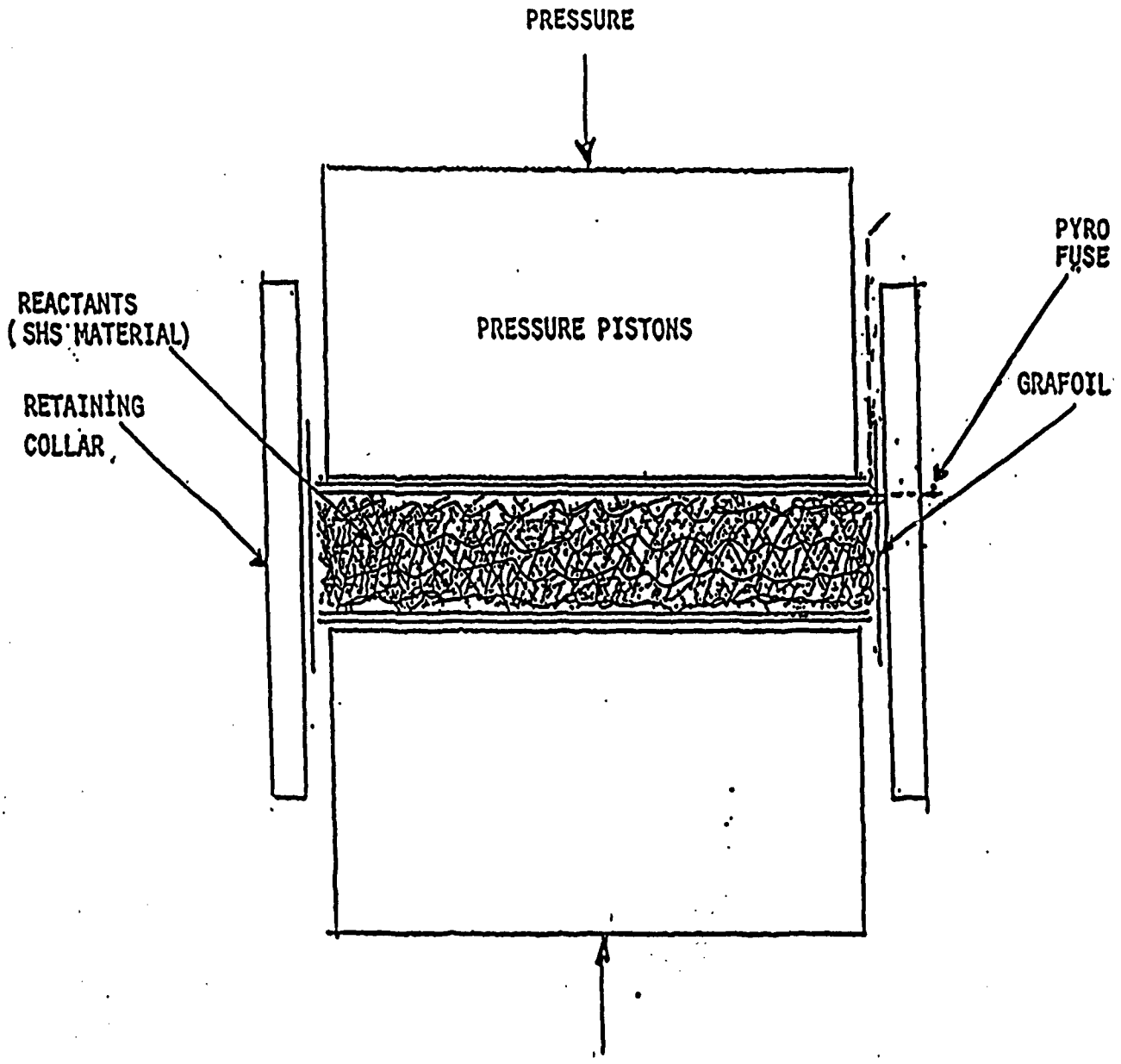
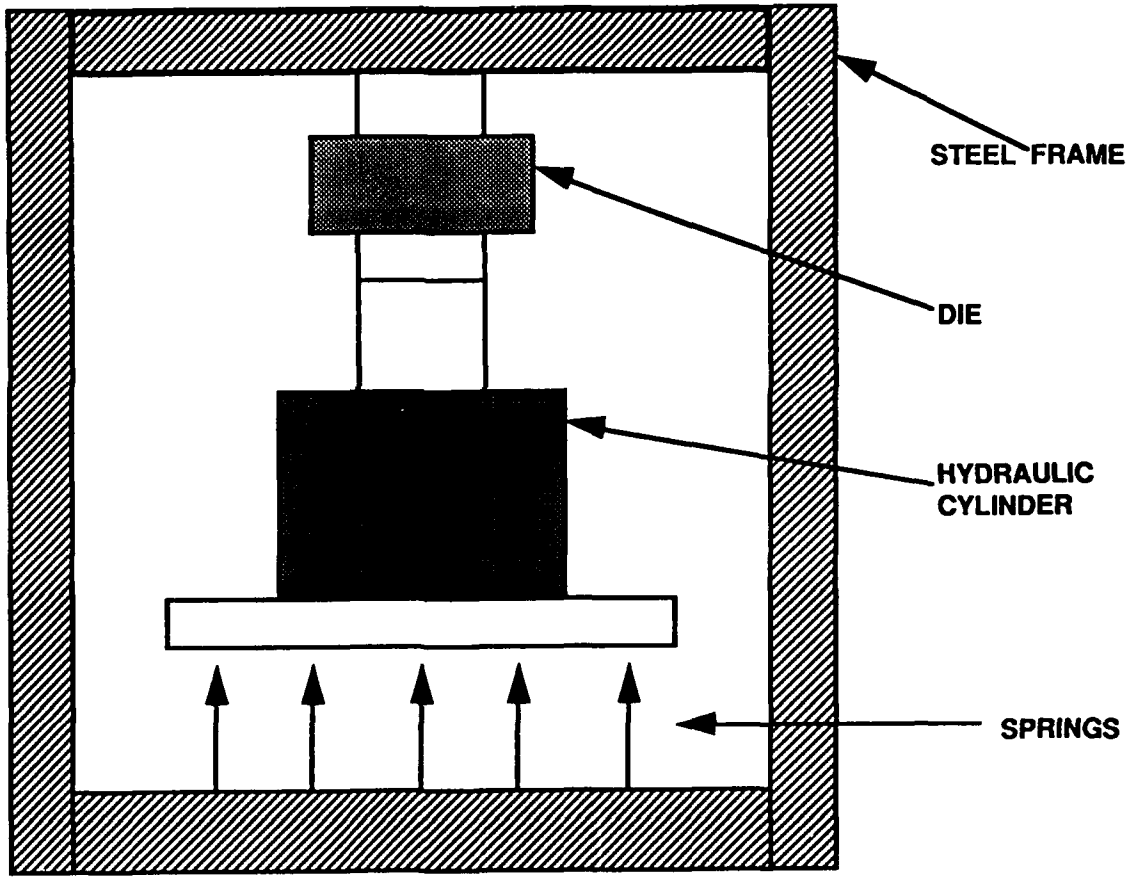


FIGURE 2. . REACTION PRESSING DIE SET-UPS USED OM SPRING LOADED PRESS.

FIGURE 3.

SCHEMATIC OF SPRING LOADED PRESS



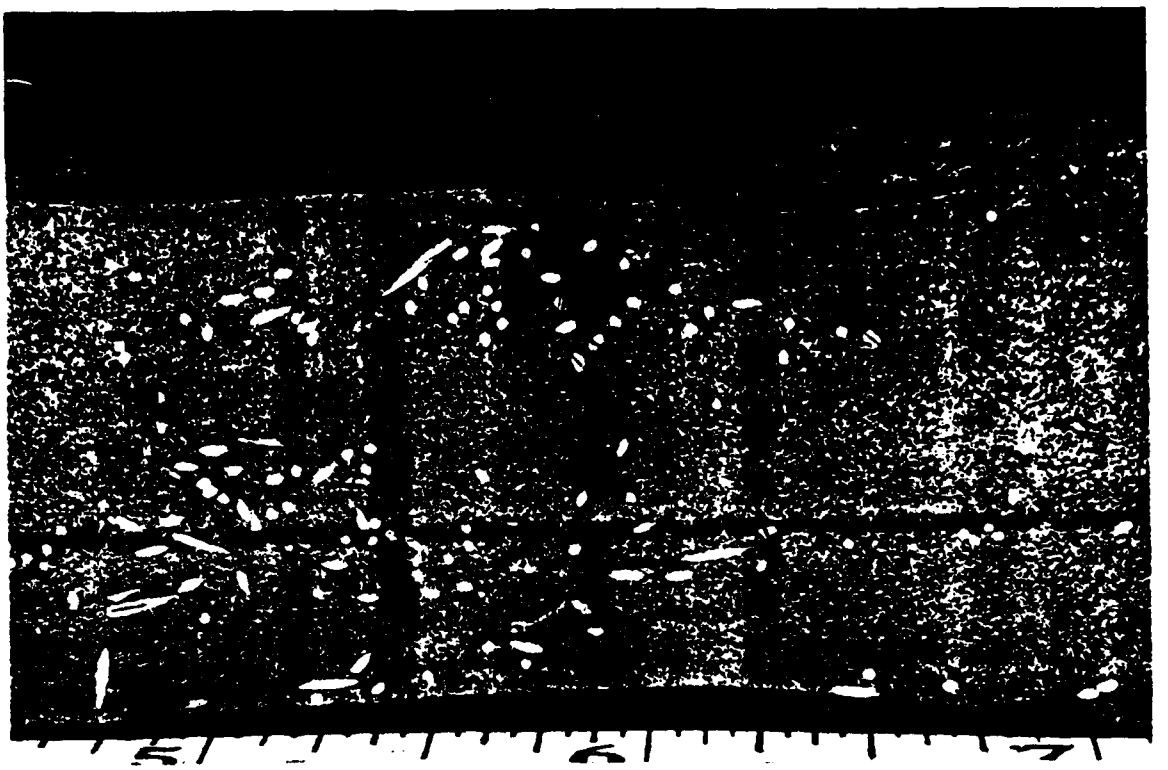


FIGURE 4. CROSS SECTION (2.2X) OF PART MADE IN EXPERIMENT 17.

REINFORCEMENT: 0.050 TUNGSTEN

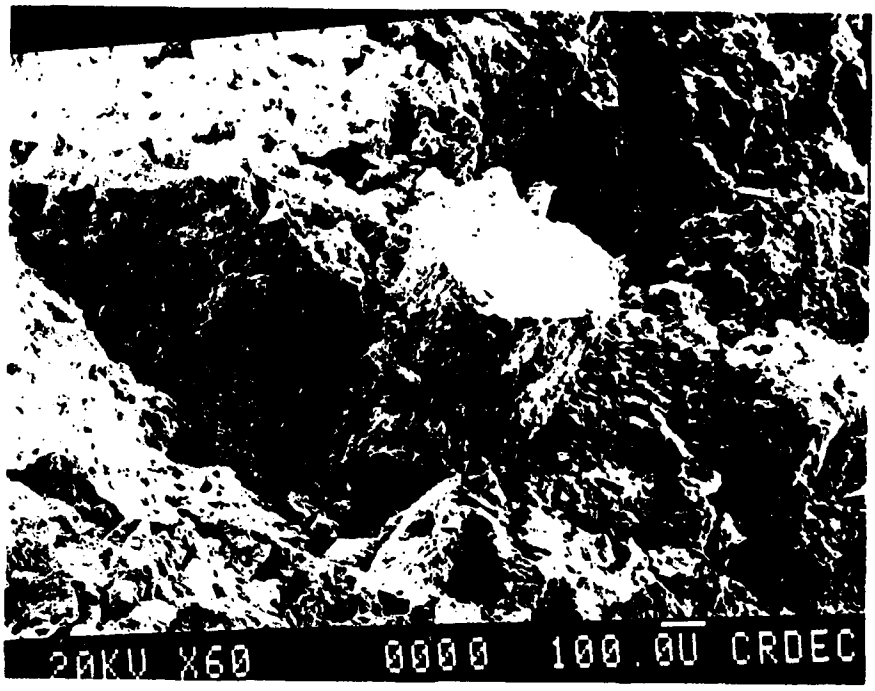


FIGURE 5. TUNGSTEN WIRE IN TiB_2 MATRIX (60X).

FIGURE 6. $TiWB_x$ WHISKERS IN THE TiB_2 MATRIX (2400X).

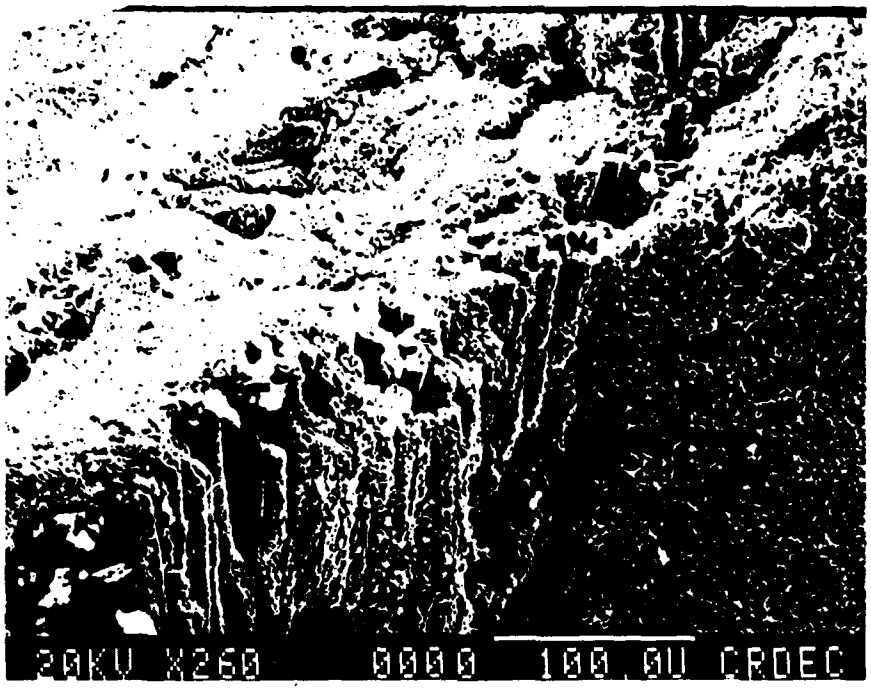


FIGURE 7. BUNDLE OF NICALON FIBERS IN TiB_2 MATRIX (260X).

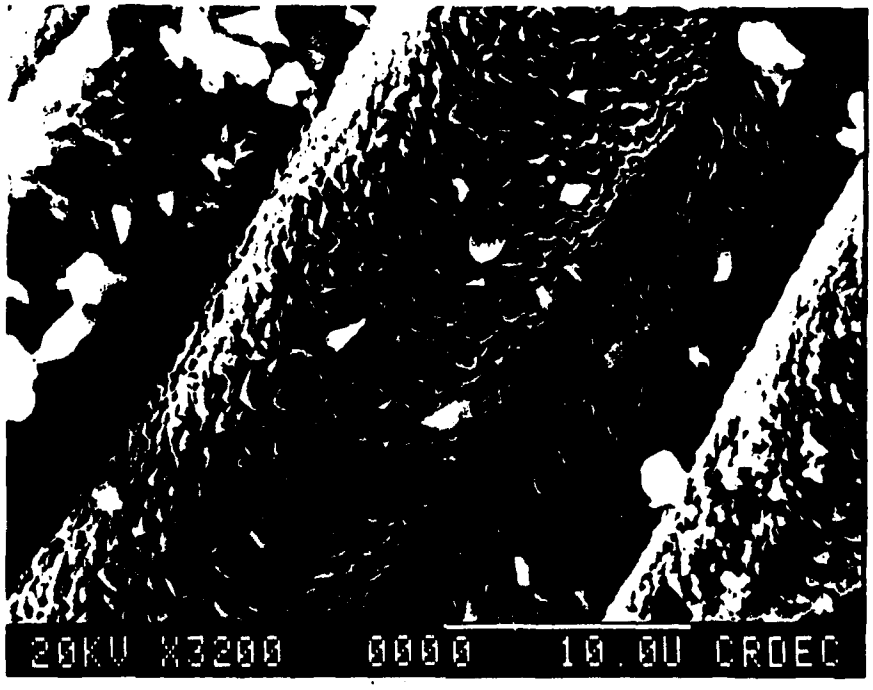


FIGURE 8. NICALON FIBERS IN TiB_2 MATRIX AFTER REACTION (3200X).

FIGURE 9. PLATE-LIKE STRUCTURES FORMED IN TiB_2 MATRIX IN NON-FIBROUS REGION (2400X).

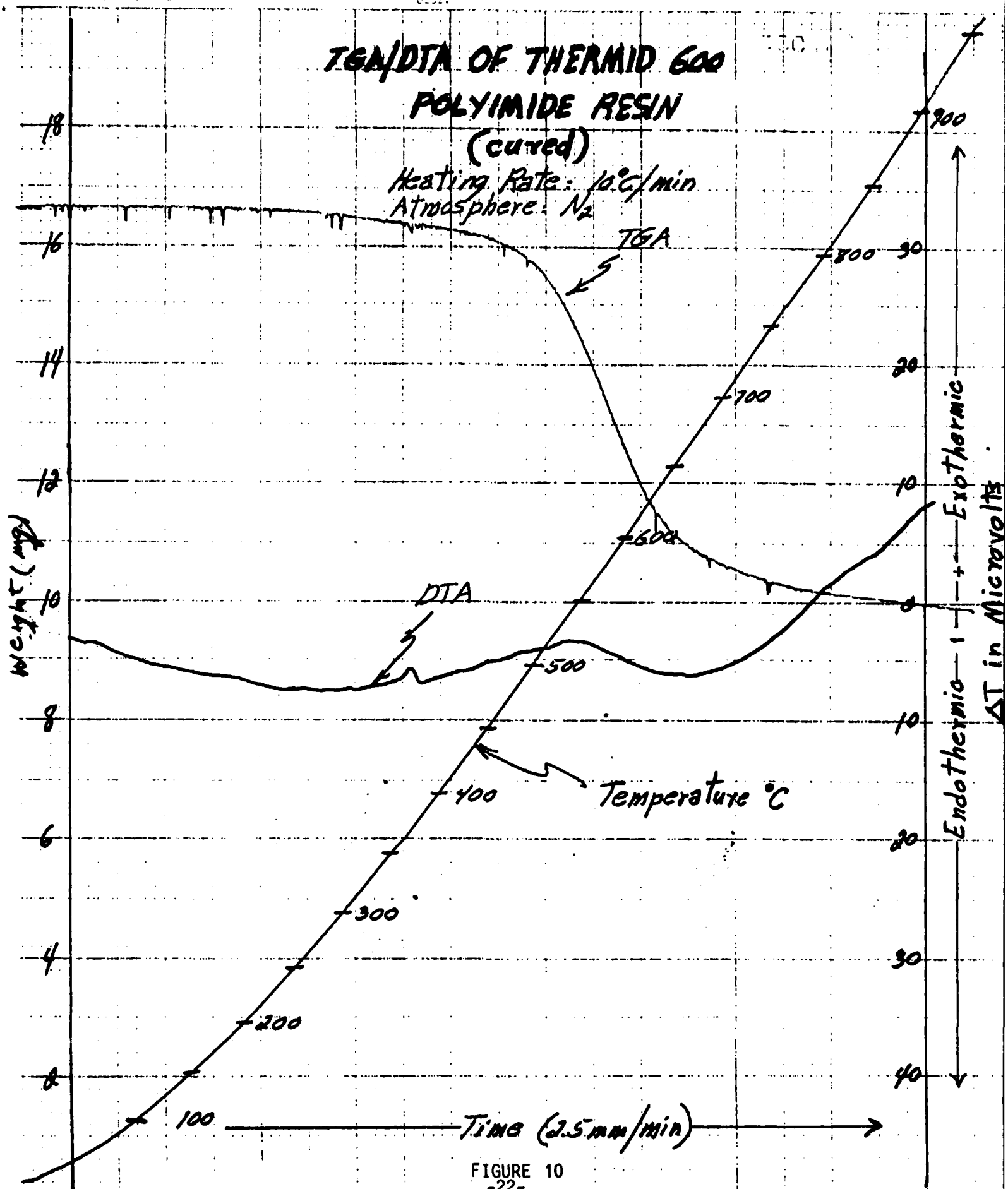

TGA/DTA OF THERMID 600
POLYIMIDE RESIN
(cured)
Heating Rate: 10°C/min
Atmosphere: N2
TGA
DTA
Weight (mg)
Temperature °C
Time (2.5 mm/min)
Endothermic — + — Exothermic
ΔT in Microvolts
18
16
14
12
10
8
6
4
2
100
200
300
400
500
600
700
800
900
30
20
10
0
10
20
30
40

FIGURE 10