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THERMAL PROTECTION USING VERY HIGH TEMPERATURE CERAMICS

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INTRODUCTION

Thermal barrier coatings sprayed by Plasma gun and monolithic structures sprayed from high temperature ceramics and refractory metals are possible utilizing a proprietary plasma gun system capable of melting virtually any material in existence. Materials can be sprayed mixed with other materials, in gradated proportions or in pure form. With this technology, critical parts such as insert coated jet engine turbine blades, fuel nozzles, combustor cans, rocket nozzles, and "stealth" outer skins with embedded electronic sensors can be created or coated.

These unique ceramics, applied usually to commercially available metal structures, offer high temperature resistance, heat transfer, and abrasion/corrosion resistance characteristics without the typical drawbacks of industrial ceramics. Many are flexible, structurally non-brittle and uncommonly impact-resistant.

After ten plus years of development, advanced plasma gun sprayed ceramics technology offers practical, economical solutions to the forward-looking challenges in ultra-supersonic high altitude aircraft skins, ultra-high temperature engines, and rocket and space shuttle protective applications.

PLASMA GUN SPRAY TECHNOLOGY

PROCESS

Figures 1 and 2 show schematically the proprietary plasma gun system presently used at Supermaterials. The plasma gun design is a trade secret of Supermaterials. Therefore, the specifics of the design will not be discussed in detail. The design is based on a modified DC plasma gun. The thermal spray process uses an accelerating hydrogen plasma stream heated to temperatures greater than 35,000° F (19,500° C) and at speeds initially in excess of 12,000 ft/sec (3700 m/sec). The system consumes up to 100 KW of power to generate these requirements. Simultaneously, argon, nitrogen or helium is mixed in the plasma stream at the gun end along with a pumped stream of particles (ceramic and/or metal powders). These particles become molten or semi-molten as they accelerate toward the sprayed surface. As they hit the surface, they splat and rapid solidification occurs. Over 27 million watts per cm^2 is pumped around the gas stream. During the spraying process, the sprayed surface reaches a maximum of 300° F (150° C). Materials such as cardboard, plastic, ceramic, glass and metal can be coated because of such low surface temperatures.

The large particles sprayed from the plasma gun system become nearly teardrop in shape then splatter onto the surface, cooling instantaneously and forming lenticular platelets upon smaller nearly spherical particle layers. These layers, not the usual in conventional spray coatings, provide unique characteristics. By adjustment of over 50 control parameters, new materials can be created.

Principally with the oxides that we spray, it appears that our system knocks off the loosely attached oxygen atoms (ref. 1). Aluminum oxide, for instance, becomes more stabilized so that this ceramic no longer absorbs or gives up oxygen when subjected to oxygen enriched gases, or a hotter environment. Gases, metals and metal oxides, when subject to certain settings of our system, appear to decouple the magnetic spins of the material's atoms. Materials which are normally magnetic, become non-magnetic. Some are magnetic, but don't conduct electricity.

PROPERTIES

In the previous section, it was stated that over 50 parameters can be changed to create new materials. Adjustments of these parameters alter one or more of the following material characteristics:

oAbrasion Resistance	oCorrosion Resistance	oCatalytic Action
oThermal Insulation	oElectrically Conductive	oLubricity
oElectrically Insulative	oEMI/RFI Shielding	oHardness
oNon-Sparking	oToughness/Shock	oRefractory
oNon-Wet	oFlexible	oThermal Shock

You can heat up a metal plate coated with our plasma sprayed ceramic to near its melting point and drop it into water with no spalling, cracking, or delaminating. Stress adjusting microscopic checking may occur, but the integrity of the bond is still intact. Hitting the plate with a hammer shows no noticeable chipping or cracking.

CAPABILITIES

New material alloys can be created by mixing almost any material. Spraying high temperature materials such as hafnia is possible as long as it is available in powder form. The thickness can vary. The ceramic thickness can range from .001-.160 of an inch or a combined metal/ceramic coating in excess of an inch. The materials can be gradated. A coating can gradually transition from one material (ceramic or metal) to another. This gradient can occur from inside to outside or along a length (figure 3). By using a removable mandrel/core, a free standing monolithic structure can be sprayed-up to stand alone. External processing (i.e., diffusion coating, sintering) can be used to enhance and seal the top surface of the coating and change the strength and durability. Virtually any metal/ceramic known can be sprayed with the system. Figure 4 shows a range of materials and their melting points that are known to withstand high temperatures. Many of the materials listed already have been sprayed at Supermaterials.

Through the use of multiple axes slides and manipulators, almost any shape can be sprayed as long as it can be set in the line of sight of the spray. Some limitations exist in the spraying of inside diameters of tubes that are below 2.6 inches. Small diameter tubes are best fabricated in their entirety by spraying them up upon mandrels.

These coatings also can be adjusted to be "fluffier" (lower overall density) or can be packed tightly into a dense compact material.

APPLICATIONS

Aerospace can benefit from plasma spray technology. Critical components such as jet engine turbine blades, fuel and rocket nozzles, combustor cans and other protective skins with imbedded sensors can be sprayed. Composite structures using ceramic sprayed carbon-carbon bodies have been tested and in use for several years. Their long term durability in high temperature and pressure environments have stretched the capability of these structures. The increasing performance requirements of aerospace has created a new set of problems. Rocket motor nozzles are being pushed toward operating temperatures of 6000° F (3315° C), high pressures and severe oxidizing fuels.

Throat erosion in a rocket nozzle affects the speed, accuracy and fuel economy (hence range) of the rocket. Materials such as Rhenium (ref. 2) and carbides such as of tantalum (TaC) and Hafnium (HfC) are being coated over carbon–carbon substrates. Historically, results over carbon–carbon structures show promise, however currently do not meet the higher performance requirements. Another disadvantage is the high cost. It has been shown that plasma sprayed monolithic rocket nozzles are a possible economical solution to the rigorous imposed standards.

ROCKET NOZZLE PROGRAM

Our plasma sprayed up monolithic ceramic nozzles were compared to 21 other nozzles made of such materials as reinforced ceramic, carbon–carbon, refractory metal, graphite and ceramic nozzles (ref. 3). The nozzles were to be ultimately used for a solid staged combustion propulsion system. The solid staged combustion system combines both the oxidizer–rich and fuel–rich gases burning at 3000° F (1649° C) in a mixing chamber so they can reburn at temperatures over 5000° F (2760° C) in a mixing chamber (figure 5).

The nozzles were fabricated in sizes and shapes to produce Mach numbers from 0.1 to 1.0. When placed in a standard test motor, the nozzles were subject to a 25 second test to be followed by a 30 second test.

Table 1 and figure 6 show the results from the prefire and postfire measurements. It can be observed that our sintered plasma spray monolithic nozzles (tests 13 and 14) had no perceptible change in throat measurements. The structure exhibited no ablation. Later unauthorized tests at higher temperatures were done with similar results. Unsuccessful attempts were made to cut the nozzle in half for examination. The material was just too hard to be cut. One other nozzle we sprayed, which was not sintered, did not survive. This demonstrates the need for additional processing and working of the material after it has been sprayed.

Originally in the program we were asked to coat a carbon–carbon structure. However, we refused because we felt that the carbon–carbon portion would not survive. Our structure is slightly denser than carbon–carbon; however, it withstood the environment. Capability to operate at higher temperatures and pressures compensate for the increased weight.

CONCLUSION

The purpose of the paper is to expose the reader to a technology that may solve some of the toughest materials problems facing thermal protection for use in aerospace. Supermaterials has created a system capable of producing unique material properties. Over 10 years and many man–hours have been invested in the development of this technology. Applications range from the food industry to the rigors of outer space. The flexibility of the system allows for customization not found in many other processes and at a reasonable cost. The ranges of materials and alloys that can be created are endless. Many cases with unique characteristics have been identified and we can expect even more with further development .

References

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2. Harding, John T., Sherman, Andrew J. and Tuffias, Robert H.: *Refractory Metals For Hot Gas Valves.* Presented at the 1989 JANNAF Propulsion Meeting at Cleveland, OH, 24 May 1989.

3. Oberth, M. H. and Marchol, P. J.: *Evaluation Of Oxidizer Rich Propellant Gas Handling Materials For Solid Staged Combustion.* Report under Air Force Rocket Propulsion Laboratory Contract FO4611-83-C-0039.

Table 1. Results of Rocket Nozzle Test

TEST	MATERIAL	PLANNED DURATION SEC	ACTUAL DURATION SEC	PROPELLANT WEIGHT gm	PREFIRE, in. D_i	PREFIRE, in. D_t	PREFIRE, in. D_e	POSTFIRE, in. D_i	POSTFIRE, in. D_t	POSTFIRE, in. D_e	CHANGE D_i	CHANGE D_t	CHANGE D_e
1	Molybdenum	10	12	562.8	0.470	0.197	0.255	N/C	0.200	N/C	0	0.003	0
2	Molybdenum	40	55	1951.3	0.450	0.191	0.255	0.530	0.530	0.475	0.080	0.243	0.240
3	4D Carbon-Carbon	25	60	1335.0	0.482	0.196	0.255	0.567	0.258	0.293	0.085	0.062	0.038
4	R-512 Niobium	25	63	1401.1	0.500	0.194	0.263	0.923	0.953	0.990	0.423	0.759	0.727
5	Aremcolox 502-1400	20	24	1113.0	0.479	0.197	0.225	0.480	0.202	0.270	0.001	0.005	0.015
									-0.364	-0.156			-0.109
6	NCM	25	27	1384.0	0.490	0.190	0.259	0.495	0.223	0.266	0.005	0.033	0.007
								-0.500	-0.225	-0.270	-0.010	-0.035	-0.011
7	K-Karb	25	30	1388.6	0.464	0.191	0.244	0.473	0.357	0.274	0.014	0.166	0.030
									-0.400	-0.290		-0.209	-0.046
8	SIC/SIC	25	23	1386.0	0.460	0.171	0.161	N/C	0.700	0.244	N/C	0.529	0.083
										-0.274			-0.113
9	P.C. Washers	25	26	1379.8	0.476	0.195	0.253	0.485	0.217	0.256	0.009	0.022	0.003
10	Graphnol	25	43	1385.0	0.487	0.199	0.251	0.527	0.240	0.265	0.040	0.041	0.014
										-0.255			-0.056
11	Calcium-Infiltrated Tungsten	25	48	1389.0	0.488	0.195	0.265	0.520	0.245	0.268	0.032	0.050	N/C
									-0.248			-0.053	
*12	"Unfired" Zirconia Diffusion Coated Molybdenum	25	55	1409.0	0.470	0.209	0.290	0.484	0.227	0.299	0.014	0.018	0.009
								-0.487	-0.228			-0.017	-0.019
*13	"Fired" Zirconia Diffusion Coated Molybdenum	25	21	1400.0	0.489	0.192	0.254	0.489	0.192	0.254	N/C	N/C	N/C
*14	"Fired" Zirconia Diffusion Coated Molybdenum	40	38	2061.0	0.503	0.183	0.263	0.503	0.183	0.265	N/C	N/C	N/C
15	AB Plane PG	25	68	1760.8	0.490	0.191	0.274	0.564	0.311	0.359	0.074	0.120	0.085
								-0.584		-0.392	0.094		0.118
16	Gadolinium Fluoride (Low Temp Ox)	25	13	1801.5	0.484	0.195	0.264	0.485	0.218	0.266	0.001	0.023	0.002
17	Gadolinium Fluoride	25	52	1387.0	0.495	0.196	0.270	0.510	0.248	0.280	0.015	0.052	0.010
								-0.531			-0.036		
18	SIC-Reinforced LaB[a]	25	68	1508.2	0.490	0.200	0.269	0.504	0.261	0.280	0.014	0.081	0.011
19	SIC-Reinforced Alumina	25	38	1567.8	0.502	0.195	0.270	0.580	0.230	0.323	0.078	0.035	0.053
20	Zirconia/Zirconium	25	25	690.0[a]	0.320[a]	0.128[a]	0.173a	0.307	0.108	0.179	(0.013)[b]	(0.020)[b]	0.006
21	SIC-Reinforced	25	40	1568[c]	0.483	0.230[c]	0.260	0.642-	0.483	0.379-	0.159-	0.253	0.119-
22	Ca Infiltrated Carbon-Carbon	25	105	1818	0.472	0.202	0.257	0.612-	0.510-	0.538-	0.140-	0.308	0.281-
								0.822	0.522	0.740	0.350		0.483
23	Hafnia/SIC/Graphnol	25	120+	1542.8[d]	0.478	0.173	0.248	0.615	0.390	0.457	0.137	0.217	0.209
24	Hafnia/Hafnium	25	10+ 60+	1719.2	0.492	0.195	0.260	0.478	0.274[e]	-[f]	-0.014	0.079[e]	-[f]

[a] Throat originally sized for low temperature oxider.
[b] Diameters shrank due to swelling of material.
[c] Throat was larger than desired, therefore grain was modified for increased surface area.
[d] Throat was smaller than desired, therefore grain was modified for decreased surface area.
[e] Throat area actually was gone. This is the minimum reading of what is left.
[f] Latter third of nozzle missing.

* COATING TECHNOLOGY DEVELOPED BY L. WILLIAM SAHLEY

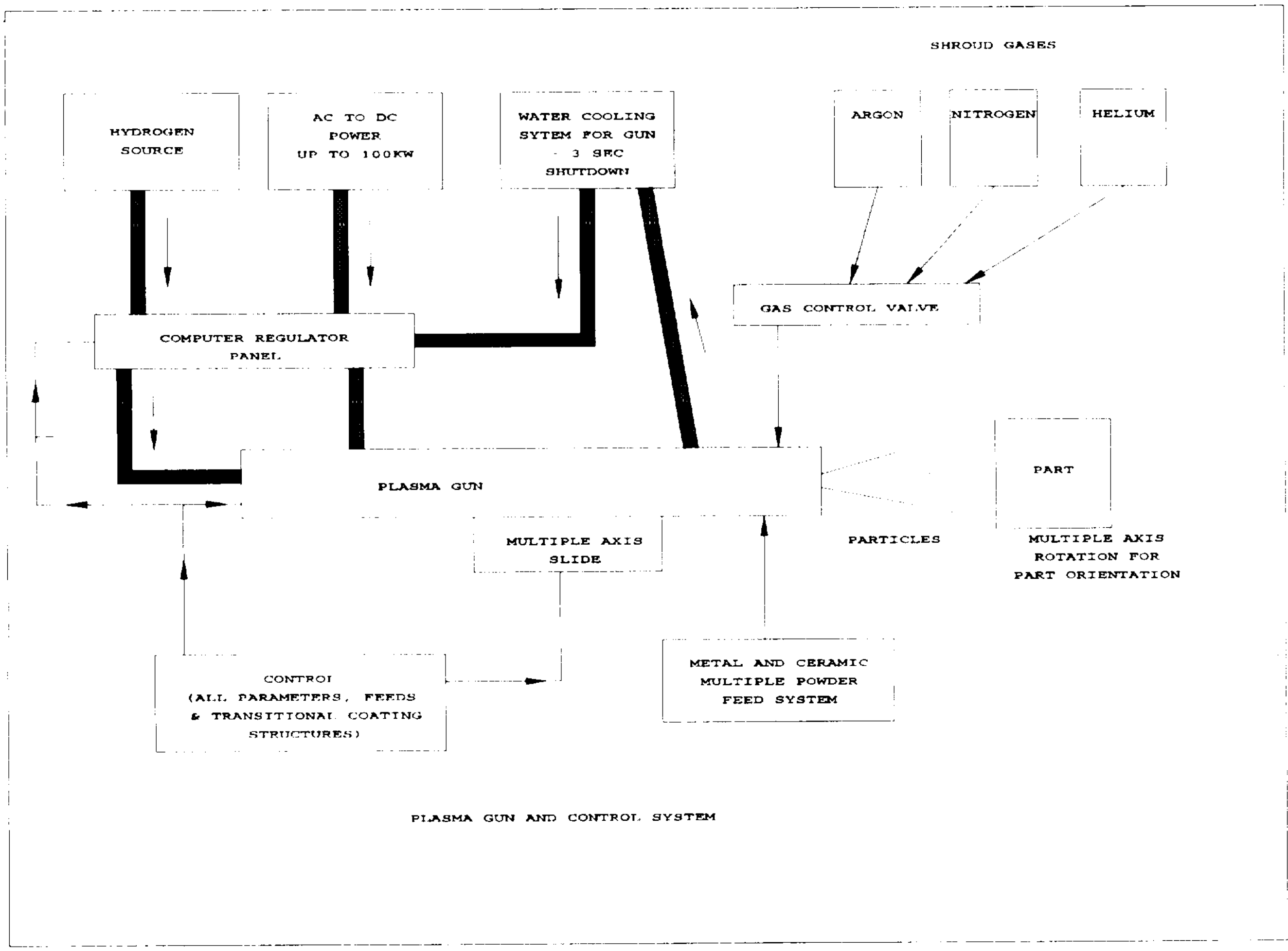
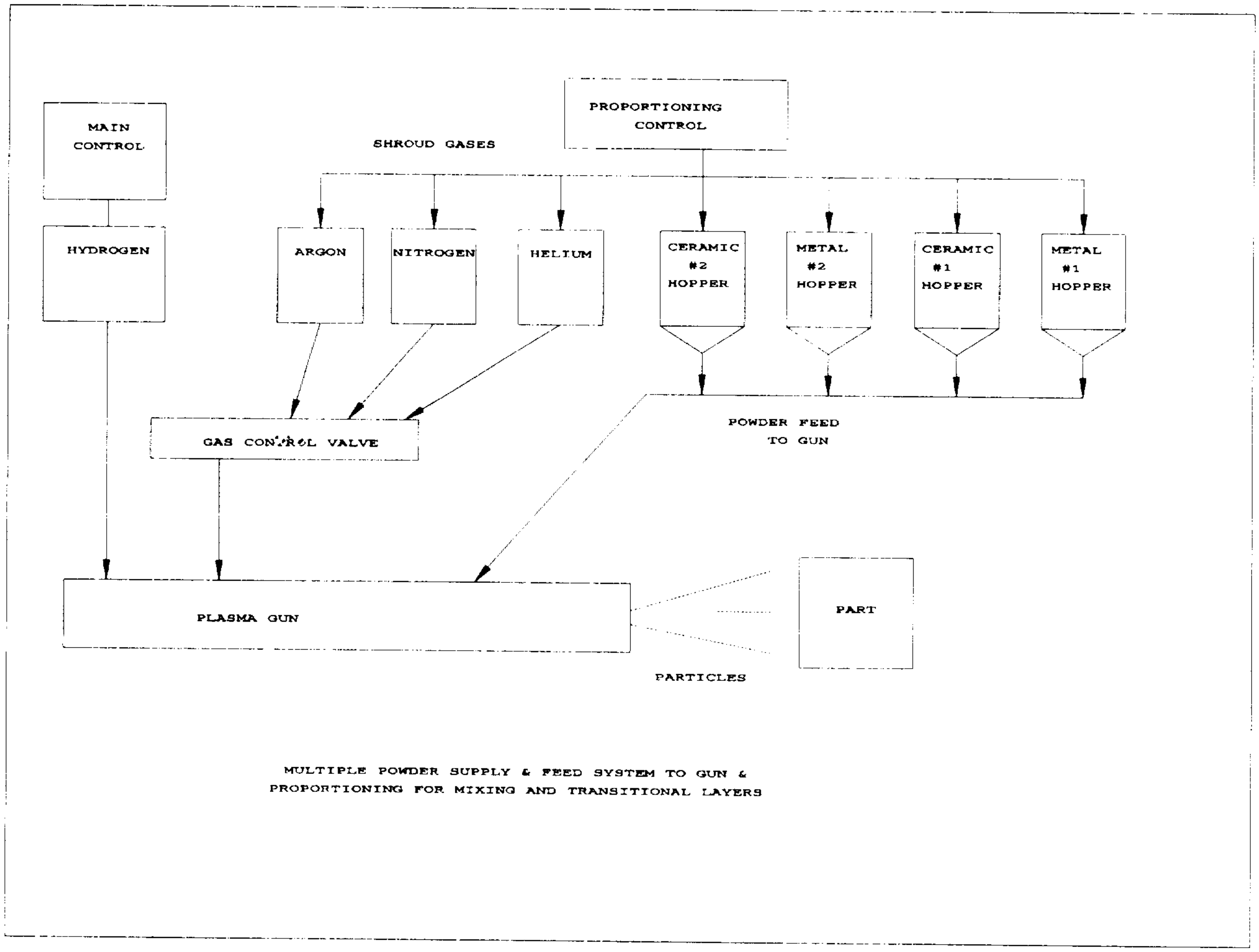


Figure 1. Plasma Gun System Schematic



MAIN CONTROL
PROPORTIONING CONTROL
SHROUD GASES
HYDROGEN
ARGON
NITROGEN
HELIUM
CERAMIC #2 HOPPER
METAL #2 HOPPER
CERAMIC #1 HOPPER
METAL #1 HOPPER
GAS CONTROL VALVE
POWDER FEED TO GUN
PLASMA GUN
PART
PARTICLES
MULTIPLE POWDER SUPPLY & FEED SYSTEM TO GUN &
PROPORTIONING FOR MIXING AND TRANSITIONAL LAYERS

Figure 2

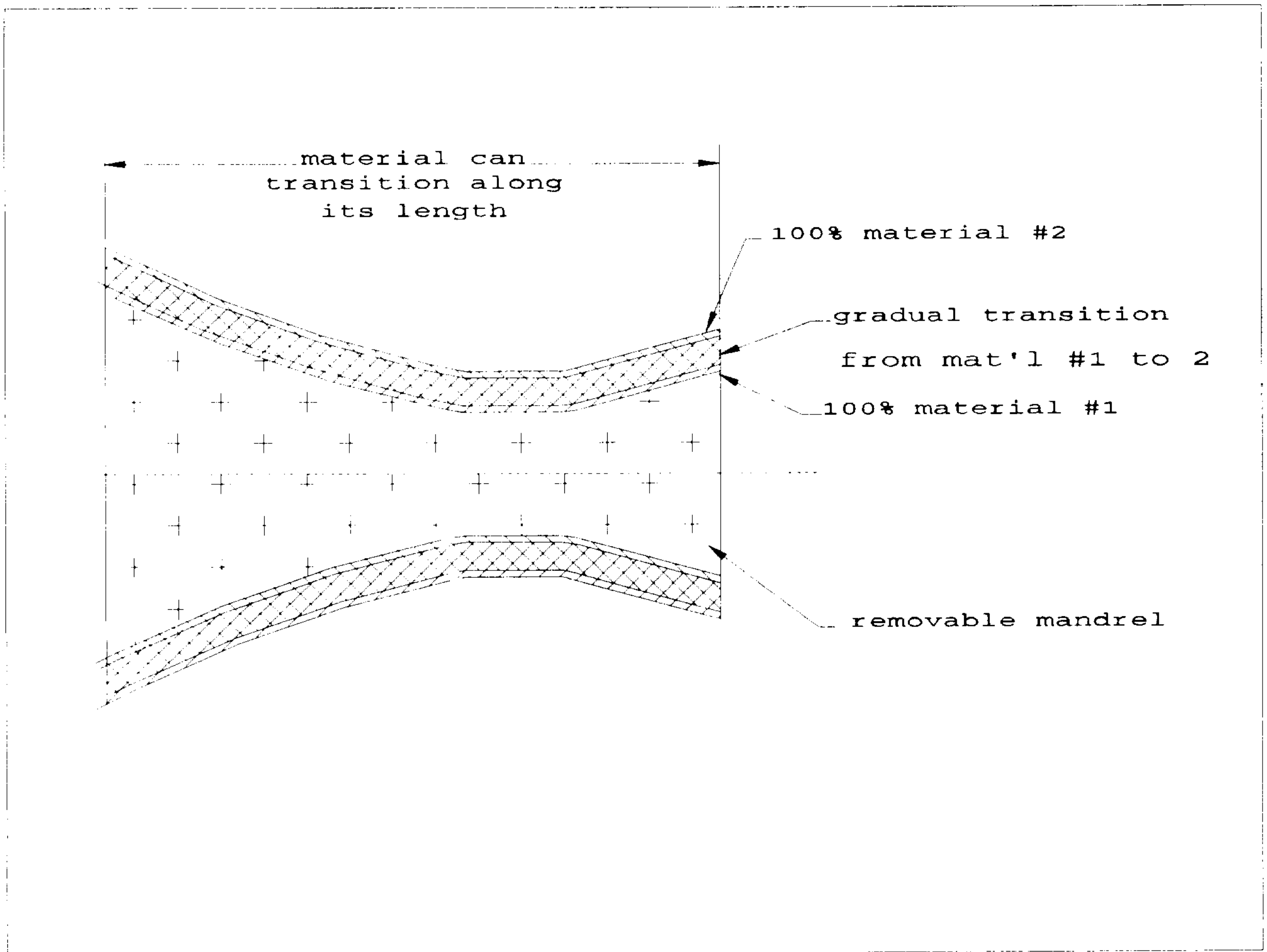
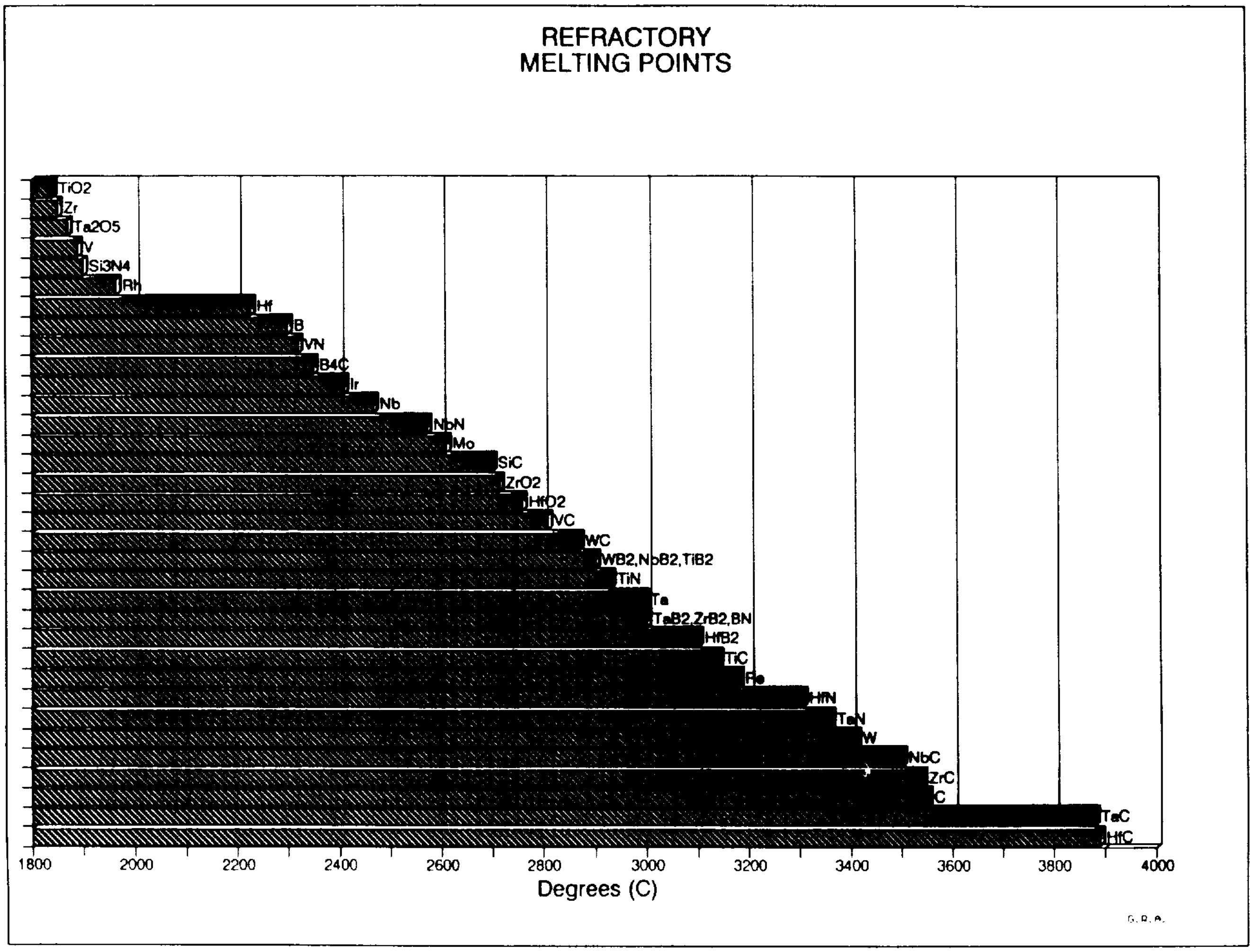
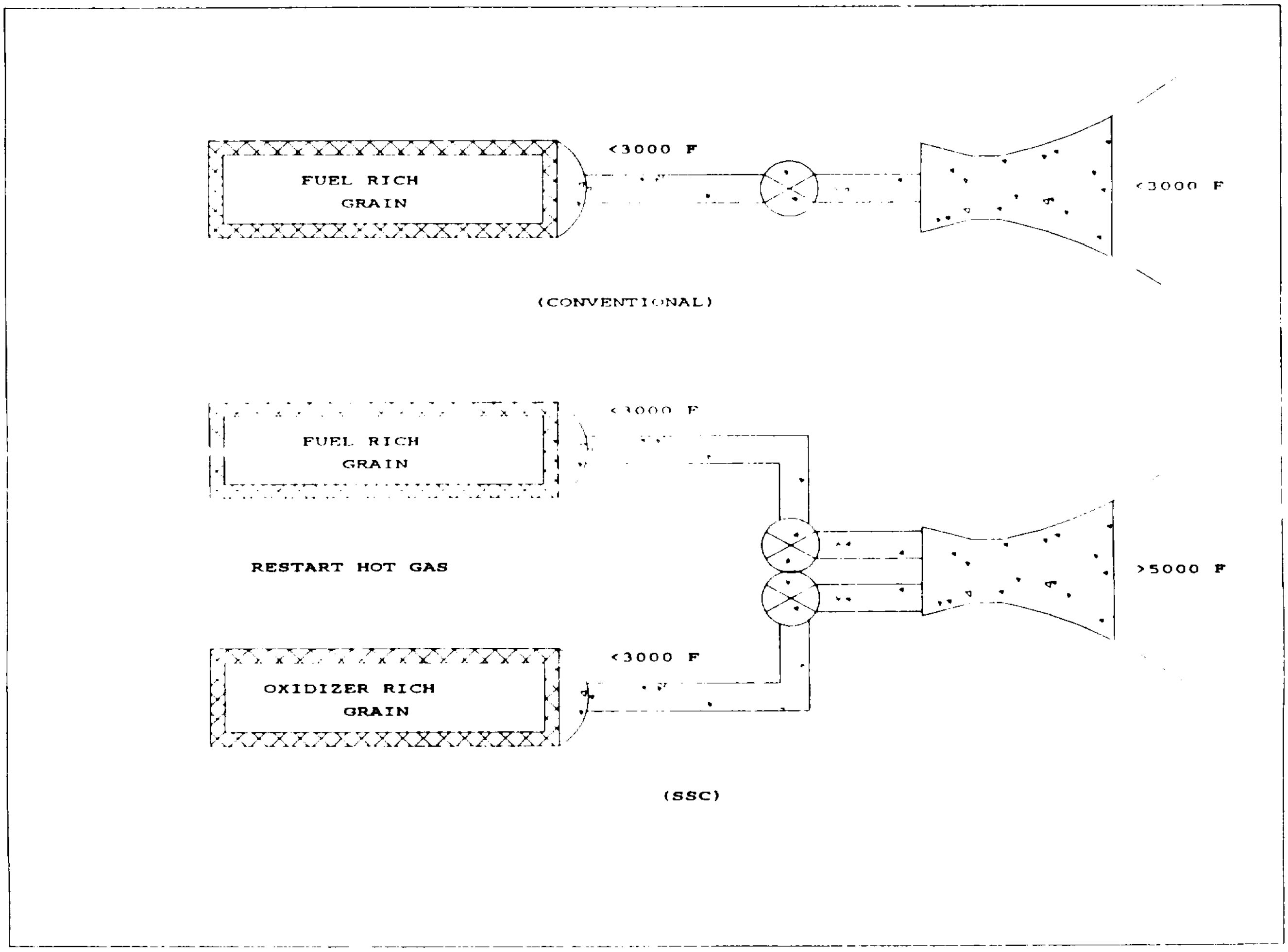


Figure 3. Plasma Sprayed Monolithic Structure



REFRACTORY
MELTING POINTS
TiO2
Zr
Ta2O5
V
Si3N4
Rh
Hf
B
VN
B4C
Ir
Nb
NbN
Mo
SiC
ZrO2
HfO2
VC
WC
WB2,NbB2,TiB2
TiN
Ta
TaB2,ZrB2,BN
HfB2
TiC
Re
HfN
TaN
W
NbC
ZrC
C
TaC
HfC
1800
2000
2200
2400
2600
2800
3000
3200
3400
3600
3800
4000
Degrees (C)

Figure 4



FUEL RICH GRAIN
<3000 F
<3000 F
(CONVENTIONAL)
FUEL RICH GRAIN
<3000 F
RESTART HOT GAS
>5000 F
OXIDIZER RICH GRAIN
<3000 F
(SSC)

Figure 5

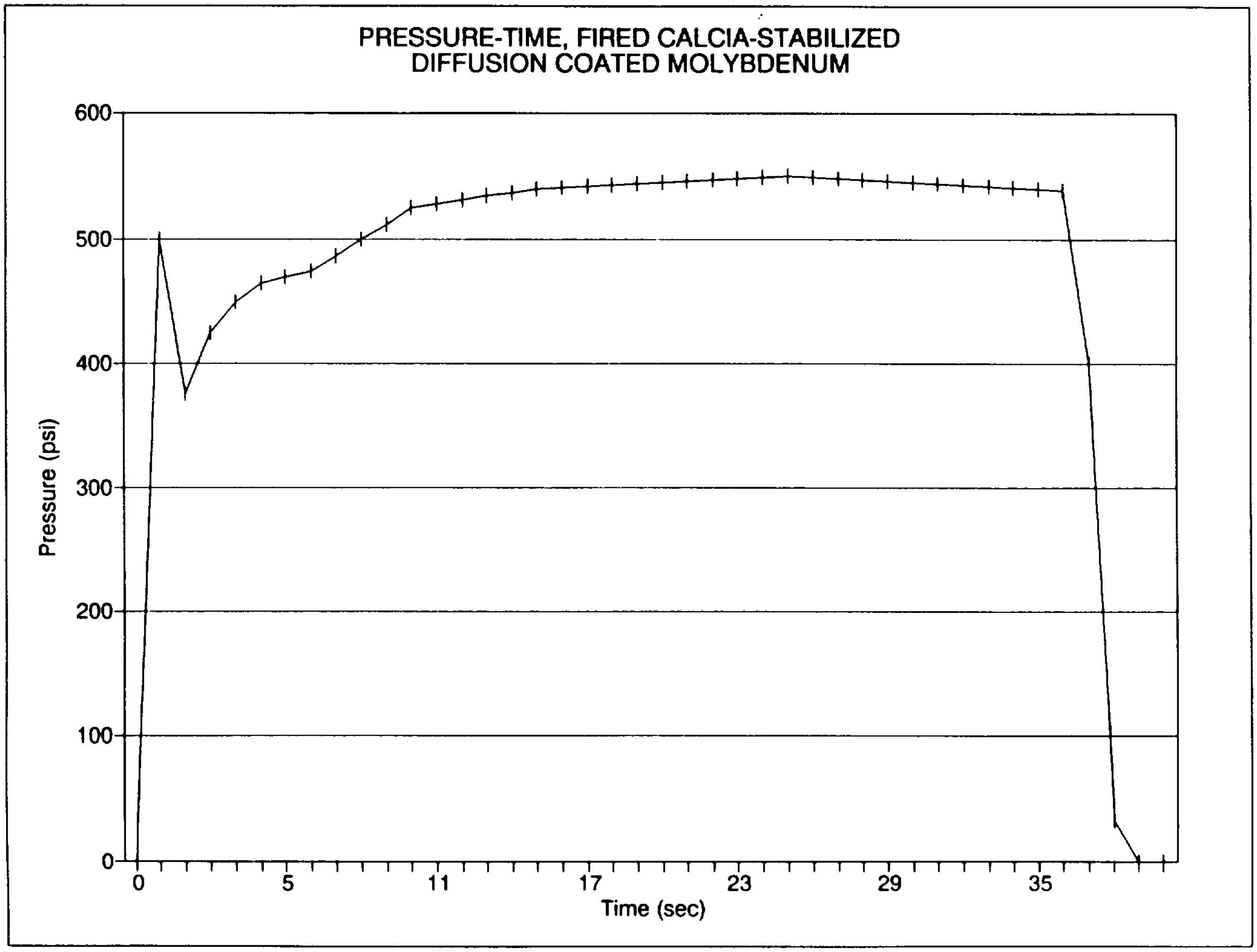

PRESSURE-TIME, FIRED CALCIA-STABILIZED
DIFFUSION COATED MOLYBDENUM
600
500
400
300
200
100
0
Pressure (psi)
0
5
11
17
23
29
35
Time (sec)

Figure 6