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THE DEVELOPMENT AND LABORATORY TESTING OF LOW Z REFRACTORY COATINGS FOR FUSION REACTOR LIMITERS*

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ABSTRACT

A materials development program for low Z (Z < 24) coated tokamak limiters is described. A variety of refractory coatings applied by chemical vapor deposition, plasma spraying and chemical conversion to graphite and copper substrates have been evaluated. The results of laboratory testing for low energy hydrogen ion erosion, arc erosion and thermal fatigue by pulsed electron beam heating are reported. The 250 V hydrogen ion erosion data, analysed in terms of the effect on plasma radiation losses from resultant contaminants, indicates near equivalence of the very low Z (B and B_4C e.g.) and the moderate Z (e.g., TiB_2) coatings. Thermal fatigue testing has identified several candidate materials which can survive 1000, 3 kJ/cm^2 pulses of electron beam heating. The development of prototype limiters of TiB_2, TiC and B coated graphite for testing in the ORNL ISX-B tokamak is described.

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INTRODUCTION

The surface in a magnetically confined fusion reactor chamber which experiences the most intense interaction with the plasma is that of the limiter. It must resist the combined effects of extreme thermal excursions and ion and arc erosion without undue contamination of the plasma. To optimize the properties of the surface for this function, a program of coating development and testing [1-4] is being carried out which has lead to the fabrication of prototype coated limiters for controlled exposure and response evaluation in the ISX-B ORNL reactor.

The materials program has consisted of coating and substrate selection (including technique of coating application), materials and process development, structure and property characterization and laboratory testing of the materials for ion and arc erosion rates and thermal shock and fatigue resistance. The limiter development program included limiter design, thermal and stress response modelling, limiter fabrication and processing and laboratory thermal pulse testing prior to the testing in the ISX-B device with the cooperation of the ORNL Fusion Energy Division.

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MATERIAL SELECTION AND FABRICATION

Greatest emphasis has been placed on material candidates for radiation cooled limiters for which peak surface temperatures near 2300K may be expected in normal operation. Thus, graphite and refractory metal substrates with boron or refractory carbide, boride and nitride coatings constitute the candidates [4]. To a more limited extent, water cooled designs have been considered with copper as the base material and with the same refractory coatings or a borided vanadium cladding to provide the low Z surface. With either limiter design, a minimum coating thickness of a few tens of micrometers is desired to provide an adequate erosion lifetime. Chemical vapor deposition provides practical deposition rates for this coating thickness and a base technology exists for a number of the carbides, borides and nitrides of interest. Plasma spraying offers a versatile technique for depositing greater thicknesses (x10) if the porous character of the coatings can be shown to be acceptable.

The immediate goal of the materials development is to provide coating/substrate combinations which can endure thousands of cycles of pulsed energy input at 2kJ per cm^2 per pulse with pulse durations of ~1 sec. and repeat times of 3 to 5 minutes [5]. This performance must be obtained with coatings selected for favorable ion and arc erosion characteristics.

Relative ion erosion yields of a variety of candidate coatings have been determined using a Kaufman ion source [4,6,7]. The source provides an intense (up to 1 mA/cm^2), uniform ($\pm$ 10% of mean) beam of mixed (H_1^o, H_2^o, H^+, H_2^+, H_3^+), but quite reproducible, ion species at extraction voltages from 50 V to 1800 V. Erosion rates determined

by weight loss for a variety of coating materials and some substrate materials for comparison are shown in Table I. In current devices arc erosion is thought to contribute appreciably to plasma contamination. Therefore, arc erosion data from laboratory experiments [4,8,9] has been collected for the candidate coatings and ~~are~~ presented in Table I. These results are obtained from weight loss after numerous arcing discharges of samples immersed in a low energy hydrogen plasma with an external magnetic field supplied to enhance the plasma formation and to cause arc movement. Measurement of total current passed in the arcs allows erosion rates to be expressed as atoms per electron.

Taking the ion erosion rates as proportional to the plasma contamination levels that could be expected for the various coatings on a limiter in a given reactor environment one can compare the coatings' relative effects on plasma power losses. To do this, we utilize the empirical relation developed by Hopkins [10] for the Z dependence of the critical concentration of plasma impurity δ^i_{max}, that would prevent ignition (power losses from radiation and thermal conduction equal to power gain from ohmic heating and α particle energy) at steady state in a power reactor:

$$\delta^i_{max} = K \times 10^{-0.1\ Z_i}$$

If more than one impurity species is present, we assume that the non-ignition criterion is reached when $\sum^i \frac{\delta^i}{\delta^i_{max}} = 1.$

Then taking the δ^i values as proportional to the product to the ion erosion yield Y_{ab} for a compound and the atomic fraction of the element

the compound, f_a or f_b, we define a parameter R_{ab} which represents the fraction of the critical contaminant concentrations for non-ignition.

$$R_{ab} = \left(\sum^{i} \frac{\delta^i}{\delta^i_{max}}\right)_{ab} = CY_{ab}\left(f_a \times 10^{0.12Z_a} + f_b \times 10^{0.12Z_b}\right)$$

By arbitrarily choosing Mo as a medium Z limiter material which would in some configuration erode to an extent which would just cause non-ignition ($R_{Mo} = 1$) one can use its erosion rate to solve for the constant C. For 250 V hydrogen ion erosion C is 0.16 and for 1000 V ion erosion it is 0.017.

Values of R_{ab} are given in Table I for coatings listed in order of Z(Avg.). For 250 V ion erosion R_{ab} is not controlled solely by atomic number. This is probably the result of chemical erosion effects and the ion energy being close to the threshold level for sputtering for some compounds. For the 1000 V data, the parameter does correlate somewhat better to atomic number. In either case, one can see no strong argument for eliminating from consideration any of the top dozen materials.

The coating/substrate combinations which have been studied in this program are listed in Table II. They were chosen for a variety of reasons including erosion acceptability, refractory character (melting point and vapor pressure), coating/substrate compatibility and thermal expansion match and the maturity of the coating application technology. Some examples of the coatings obtained are shown in Figures 1a, b and c. The chemical vapor deposited coatings on graphite are typified by the microstructure of TiB_2 on Poco AXF-5Q shown in

Figure 1a. The coating appears fully dense, well bonded to the substrate and uniform in structure and thickness. Figure 1b shows a typical plasma sprayed coating, TiC on copper. The porous nature of these coatings (20-30% porosity) is apparent. Despite their thickness (200 μm) they are quite resistant to thermal shock by virtue of their distention. The explosively clad vanadium copper with a thin, 15 μm, chemical conversion coating of VB_2 is shown in Figure 1c. The vanadium thickness has been scaled to allow maximum energy input without exceeding temperature limits at either the VB_2/V or V/Cu interface [17].

All coatings were extensively characterized [18] for chemical purity, stoichiometry, crystal structure, preferred orientation and emissivity. In addition, residual stress and thermal expansion measurements [4] have been made on the CVD TiB_2 and mechanical property (elastic modulus and fracture strength vs. temperature) studies have been completed on the CVD TiB_2 and CVD boron [18].

THERMAL FATIGUE STUDIES

Six of the developmental materials in Table II were selected for thermal fatigue testing [19] in a program sponsored by Princeton Plasma Physics Laboratory [20]. Two clad copper materials under development at Argonne National Laboratory [21] were also tested. Testing was done by electron beam pulsed heating and conducted in the test stand shown in Figure 2. The apparatus incorporates a 30 kW, 30 kV electron gun with a rastered (1000 Hertz) beam, a 32 sample motorized stage with computer controlled indexing of samples, TV monitoring of samples for damage, optical pyrometer tracking of surface temperature,

thermocouple recording of rear surface temperature and residual gas analysis of evolved species. Four 2.54 x 2.54 x 1.27 cm samples each of eight materials were exposed to 200 cycles of 1.5 sec. pulses of 1 kW/cm^2 incident energy density over the full surface area at a repeat time of 320 sec. The square samples rested over 2.87 cm diameter holes in a graphite plate so that cooling was largely by radiation. It is expected that approximately 20% of the incident energy is back scattered. Another set of samples was tested at 2 kW/cm^2 of incident energy density (all other conditions repeated) with the samples resting on a water cooled copper plate. Four materials were selected from the original eight and subjected (in multiples of eight) to 800 additional cycles of 2 kW/cm^2 with water cooling. Thus four samples of each material saw a total of 1000 cycles and four saw 800 cycles. In all tests, when a failure of a given sample was observed further electron beam pulses were cancelled. The peak surface temperatures measured after many cycles at the end of the electron beam pulse and the rest temperatures (at the end of the rest period) are shown in Table III.

Table III summarizes the results of all tests and Figure 3 shows the surface appearance of the 800/1000 cycle samples. In the 200 cycle tests, almost all of the materials survived without obvious damage. Two of the explosively clad samples suffered melting of the cladding. This was apparently the result of poor bonding to the copper substrate. The samples were taken from edge of the plate where bonding is unreliable [22].

After the 800/1000 cycle exposure, the chemical vapor deposited TiC on graphite had little evidence of coating damage. The plasma sprayed TiB_2 on copper also appeared sound with only a discoloration of the outer layer and some loss of this layer at the edge of the sample. The CVD TiB_2 on graphite had a blue deposit around the edges which is thought to be a species evolved from the coating at high temperature (probably associated with Cl and O impurity) which deposits on the cooler surrounding samples. Deposition conditions are now being varied in an effort to correct the impurity problem. Late in the testing, several of the TiB_2 samples also developed a shiny area in the center of the sample which, pending further investigation, is thought to represent surface melting related to carbon interdiffusion and/or altered stoichiometry related to the suspected evolved Ti-Cl-O species. Only the borided vanadium clad copper exhibited a clear failure which is probably inherent to the material type. The samples exhibit pronounced expansion of surface regions, "thermal ratcheting," plus subsurface melting and, in several instances, protrusion of melt through to the surface. Warpage of the sample drastically reduced contact with the water cooled copper table. Considerable interdiffusion is indicated which after prolonged exposure leads to the formation of ternary or quarternary compositions of lower melting point. This material is thus indicated to have severe limitations which would make it useful only under conditions of more effective active cooling.

PROTOTYPE LIMITER DEVELOPMENT

Parallel with the materials development, a program for the development of coated limiters for testing in the ISX-B reactor at

ORNL has been carried out. This testing program and the initial results are reported in separate papers [23,24]. The limiters (Figure 4) are of mushroom shape with a thick threaded stem for support by a copper cup which has provision for water cooling of the base and for heating for bake-out in a pre-evacuation chamber. Limiters prepared for the initial series of experiments had 10-15 μm coatings of CVD TiC, TiB_2 or boron on a Poco AXF-5Q graphite limiter. A 304L stainless steel limiter was also fabricated for comparative testing. Thermal stress modelling of the TiB_2/graphite limiter has been reported [4]. Initial results of tests of the TiC and TiB_2 coated limiters are very encouraging with the former exhibiting the least effect of the exposure.

SUMMARY

A variety of low-Z (Z < 24) coated materials have been developed for application as limiters in tokamak fusion reactors. The principal effort has been devoted to chemical vapor deposited coatings of TiC, TiB_2 and boron on graphite for the radiation cooled limiter concept. Analysis of ion erosion data on the basis of the effect of erosion on plasma radiation losses indicates near equivalence of candidates. Thermal fatigue testing by both electron beam and ion beam pulsing have demonstrated survival of several candidates to the levels of exposure anticipated for the TFTR reactor. Initial testing of prototype limiters in the ORNL ISX-B reactor have also produced favorable results with the TiC/graphite limiter exhibiting minimal damage from the exposure.

ACKNOWLEDGEMENTS

The chemical vapor deposition studies of TiB_2 and boron at Sandia National Laboratories were conducted by H. O. Pierson and his large contribution to this program is gratefully acknowledged.

REFERENCES

1. M. J. Davis, J. Nucl. Mater., 85 and 86 (1979) 1063.
2. D. M. Mattox, Thin Solid Films, 63 (1979) 213.
3. A. W. Mullendore, D. M. Mattox, J. B. Whitley and D. J. Sharp; Thin Solid Films, 63 (1979) 243.
4. A. W. Mullendore, J. B. Whitley, D. M. Mattox and R. K. Thomas; Presented to 8th Sym. on Engineering Problems of Fusion Research (IEEE) 13-16 November, 1979, San Francisco, To be published in Proceedings.
5. S. Z. Fixler, J. Nucl. Mater., 85 and 86 (1979) 241-246.
6. D. M. Mattox and D. J. Sharp, "Low Energy Hydrogen Ion Erosion Yields as Determined with a Kaufman Ion Source," Sandia Laboratories Report SAND78-1029, October, 1978.
7. D. J. Sharp, J. K. G. Panitz and D. M. Mattox, "Applications of a Kaufman Ion Source to Low Energy Ion Erosion Studies," To be published in J. Vac. Sci. Technol. (Presented to 15th Symposium on Electron, Ion and Photon Beam Technology, May 30-June 1, 1979, Boston, Mass).
8. J. B. Whitley and D. M. Mattox, "Plasma Arcing of Low-Z Coatings," Proc. of Arcing Phenomena in Fusion Devices Workshop, April 5-6, 1979, Knoxville, TN., R. V. Langley, ed., DOE Contract 7405-ENG-26.

9. J. B. Whitley and D. M. Mattox, "Erosion of Refractory Metals and Coatings by Arcing," Presented to the 1979 TNS-AIME Meeting, Sept. 16-20, 1979, Milwaukee, WI.

10. G. R. Hopkins, "Fusion Reactor Studies: Potential of Low Z Materials for the First Wall," EPRI 115-2 Key Phase Report Sept. 1975, Prepared by General Atomics Co., San Diego, CA.

11. G. R. Hopkins, "Estimation of Impurity Radiation Loss from Fusion Reactor Plasmas," Conf-72111, Symposium Proceedings Technology of Controlled Thermonuclear Fusion Experiments and Engineering Aspects of Fusion Reactors, Austin, Texas (1972).

12. H. O. Pierson, E. Randich and D. M. Mattox, J. Less Common Metals, 67 (1979) 381.

13. H. O. Pierson and A. W. Mullendore, "The Chemical Vapor Deposition of TiB_2 From Diborane, To be Presented at International Conference on Metallurgical Coatings, AVS, April 21-25, 1980, San Diego, CA.

14. L. Aggour, E. Fitzer and J. Schlichting; "TiC Coatings on Graphite by CVD," Proc. of 5th International Chemical Vapor Deposition Conf., Princeton, NJ, Electrochemical Society Publication (1975).

15. H. O. Pierson and A. W. Mullendore, Thin Solid Films, 63 (1979), 257.

16. A. A. Popoff, Mech. Engineering, 100, No. 5 (1978), 28.

17. R. K. Thomas, Pers. Comm.: Thermal Transport Calculations

18. A. W. Mullendore, "Characterization of Low Z Coated Materials for Fusion Reactor Applications," Sandia Laboratories Report SAND80-0809.

19. D. M. Mattox, A. W. Mullendore, J. B. Whitley and H. C. Pierson, "Thermal Shock and Fatigue Resistant Coatings for Fusion Reactor Environments," to be presented at International Conference on Metallurgical Coatings, AVS, April 21-25, 1980, San Diego, CA.

20. TFM Impurity Control R & D Program, J. L. Checci, Manager.

21. M. Kaminsky, "Cladded Materials for Fusion Applications," To be presented at the International Conference on Metallurgical Coatings, AVS, April 21-25, 1980, San Diego, CA.

22. M. Kaminsky: Personal Communication.

23. J. B. Whitley, A. W. Mullendore, R. A. Langley, "Testing of Low-Z Coated Limiters in Tokamaks," To be presented at International Conference on Metallurgical Coatings, AVS, April 21-25, 1980, San Diego, CA.

24. R. A. Langley, L. C. Emerson, J. B. Whitley and A. W. Mullendore, "Testing of Coated Limiters in ISX," Presented at the 4th International Conf. on Plasma Surface Interactions in Controlled Fusion Devices," April 21-25, 1980, Garmisch-Partenkirchen, FRG.

TABLE I. EROSION YIELDS AND RADIATION LOSS PARAMETER

Z_{AUG}	MATERIAL	H^+ Erosion Yield Atoms/Ion		Arc Erosion Rate-Atoms/e$^-$	R_{ab}	
		250 V	1000 V		250 V	1000 V
	Be (P.S.)[1]	.0080	.0260	1.2	.0032	.0011
	B (CVD)[2]	.0140	.0330	0	.0071	.0018
	B_4C	.0130	.0180		.0069	.0010
	VBe_{12} (P.S.)	.004	.0160	1.30	.0113	.0048
	C (AXF-5Q)	.033	.043		.0210	.0029
	BN	.023	.0230		.0150	.0016
	BeO	.013	.0270		.0092	.0020
	SiC	.0041	.0210		.0095	.0052
	TiB_2 (CVD)	.0010	.0100	0.34	.0087	.0092
	(P.S.)	.0009	.0090	1.10	.0078	.0083
	TiC (CVD)	.0014	.0094	0.12	.0182	.0130
	(P.S.)	.0008	.0080	0.48	.0104	.0110
	V	.0005	.0170		.0160	.1238
	304	0020	.0037	0.34	.1370	1.0
	Mo	.00039	.0018		1.0	770
	W	.0002			800	

1. (P.S.) - Plasma Sprayed

2. (CVD) - Chemical Vapor Deposition

TABLE II. PRIME LIMITER MATERIALS UNDER ACTIVE DEVELOPMENT

Coating	Substrate	Coating Technique	Supplier	Ref.
TiB_2	Poco[1] AXF-5Q Graphite	CVD - BCl_3 + $TiCl_4$	Sandia Laboratories	12
TiB_2	Poco AXF-5Q Graphite	CVD - B_2H_6 + $TiCl_4$	Sandia Laboratories	13
TiC	Poco AXF-5Q Graphite	CVD - CH_4 + $TiCl_4$	Ultramet[2]	14
TiC	Poco AXF-5Q Graphite	CVD - CH_4 + $TiCl_4$	MTC[3]	14
B	Poco AXF-5Q Graphite	CVD - B_2H_6	Sandia Laboratories	15
TiB_2	Cu	Plasma Spray	UC-Y-12[4]	4
VB_2	V Clad Cu	Chemical Conversion of Explosive Cladding	MRC[5] LASL[6]	16

1. Poco Graphite Inc.
2. Ultramet Corp., Pacoima, CA
3. Materials Technology Corp., Dallas, TX
4. Y-12 Division of Union Carbide, Oak Ridge, TN
5. "Borofuze" Process, Materials Research Corp., Medford, MA
6. CMB-6, *Los Alamos Scientific Laboratory*

TABLE III. SUMMARY OF ELECTRON BEAM THERMAL FATIGUE TESTING

		200 Cycle Rad'n Cooled 1 kW/cm^2		200 Cycle Water Cooled 2 kW/cm^2		1000 Cycle Water Cooled 2 kW/cm^2
		T_M/T_R	Damage	T_M/T_R	Damage	Damage
TiB_2/Poco	CVD-SNLA	1520/570K	----	2520/720K	----	Slight Surface Melt?
TiC/Poco	CVD	1520/570K	----	2520/720K	----	----
TiB_2/Cu	P.S.	1150/300K	----	1500/420K	----	Slight Edge Exfoliation
VB_2/V/Cu	CC-EB	1150/300K	----	1350/420K	----	Interdiffusion Subsurface Melt
TiB_2/Poco	CVD-MTC		----		----	
B/Poco	CVD		----		----	
V/Cu	EB		Edge Melt		----	
Ti/Cu	EB		----		Edge Melt	

KEY

CVD - Chemical Vapor Deposition

P.S. - Plasma Sprayed

CC - Chemical Conversion

EB - Explosively Bonded

T_M - Peak Surface Temperature

T_R - Rest Temperature

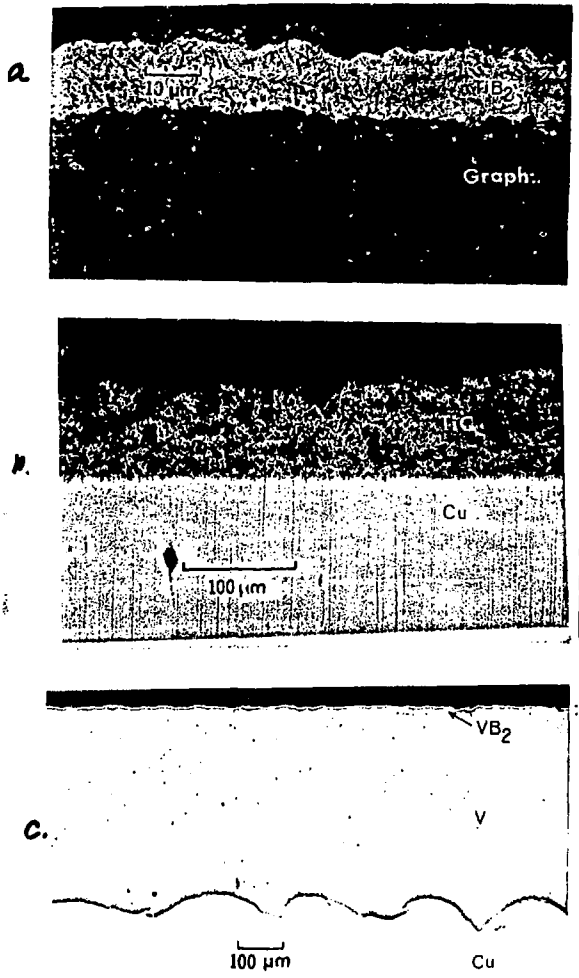

Figure 1. Microstructures of Coated Materials.

a. CVD TiB_2 on Poco AXF-5Q graphite.
b. Plasma sprayed TiC on copper.
c. VB_2 on V clad copper.

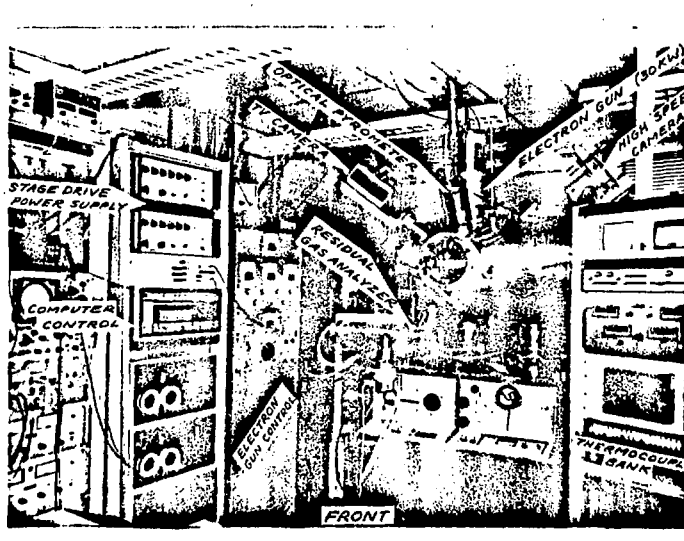

Figure 2. Combined Environment Test Chamber.

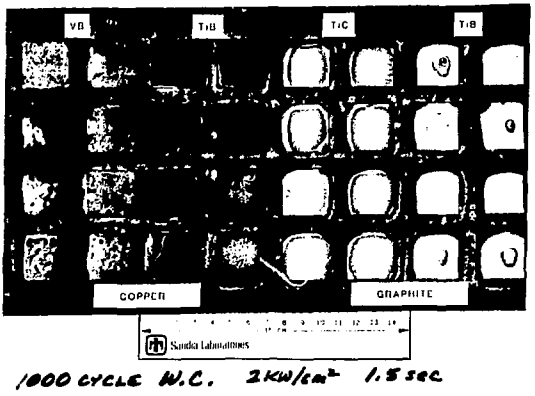

Figure 3. Coated samples after 800/1000 cycle Thermal Fatigue Test.

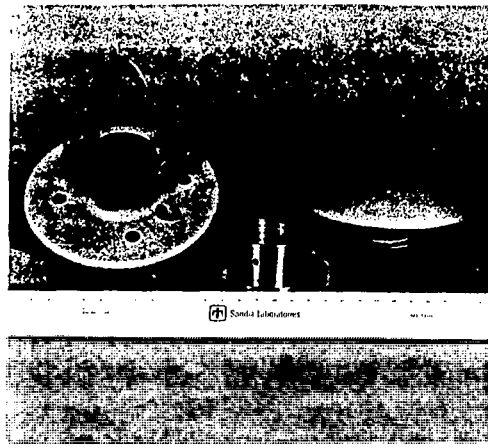

Figure 4. Coated limiters for Tokamak testing.