MASTER

SAND79-0707C

COATINGS FOR FUSION REACTOR ENVIRONMENTS*

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ABSTRACT

The internal surfaces of a tokamak fusion reactor control
the impurity injection and gas recycling into the fusion plasma.
Coating of internal surfaces may provide a desirable and possibly
necessary design flexibility for achieving the temperatures, ion
densities and containment times necessary for net energy pro-
duction from fusion reactions to take place. In this paper the
reactor environments seen by various components are reviewed
along with possible materials responses. Characteristics of
coating-substrate systems, important to fusion applications,
are delineated and the present status of coating development
for fusion applications is reviewed. Coating development for
fusion applications is just beginning and poses a unique and
important challenge for materials development.

INTRODUCTION

Controlled thermonuclear reactors (CTR's) pose a unique and demanding environment for materials. At the present time, magnetic confinement of heated plasmas, particularly the tokamak configuration, is closer to achieving a useful controlled fusion reaction than are the inertial confinement configurations. Figure 1 depicts the design of a tokamak reactor - with its attendant internal components. The D + T plasma is confined by magnetic fields and is heated by passing large currents through the plasma and injecting high energy (~100 KeV) neutral hydrogenic particles which give up their energy to the plasma particles by collisions. Wall armor, opposite the neutral beam injectors, absorbs the "shinethrough" of energetic particles which are not thermalized by the plasma. The wall armor may cover 20-30% of the interior's wall surface. After the ignition temperature is reached, the plasma is heated by the alpha particles produced by the D + T reaction.

The chamber wall is called the first wall and maintains the vacuum integrity of the system and allows the penetration of the 14 MeV neutrons from the D + T reaction into the energy absorber and heat transfer medium. The wall is also subjected to bombardment by those D, T and alpha particles which are not confined by the magnetic field. The wall surfaces affect the injection of contaminants into the plasma and the recycling of contaminants and hydrogenic species between the plasma and the wall. Plasma impurities result in plasma cooling from line and Bremstrahlung radiation, increase the gas-kinetic pressure,

prevent neutral beam penetration into the core of the plasma, initiate runaway electrons (a "fault" condition) and affect sputtering and arc erosion. In gas recycling, the low energy plasma ions and neutrals impinge on the internal surfaces and are returned to the plasma by reflection or absorption and desorption. If energy is lost by the particles in this process, the plasma is cooled. Gas recycling from the walls in the neutral beam injectors can reduce the neutral beam output. The immediate goal in a controlled D + T reaction is to obtain ion temperatures of 5-10 KeV and a $N\tau$ of 10^{14} sec/cm^3 where N is the ion density and τ is the confinement time.

Limiters are used to prevent the plasma from striking the wall. Some tokamak designs do not use isolated limiters but use "bumper" limiters on the wall. Not shown in Figure 1 are divertors which are used in some designs. The divertors use a magnetic field to divert the outermost layer of plasma into a region external to the main vacuum vessel where the high energy plasma particles can impinge on surfaces and be removed without introducing impurities into the plasma.

Table 1 gives typical environments seen by the various components under normal operating conditions of a 200 MJ reactor and under the fault (abnormal-undesirable) conditions of beam disruption and runaway electrons. These values are nominal and can be expected to vary greatly. Table 2 indicates the possible responses of the components to the environments listed in Table 1.

In addition to the survivability of the components, a major concern to achieving a controlled fusion reaction is plasma cooling by impurities and gas recycling. High Z contaminants

are more detrimental to plasma ignition and temperature than
are low Z contaminants.[1] Contaminants may arise from residual
gases, (N_2, O_2, H_2O, CO, etc.), absorbed contaminants (H_2O, CO,
hydrocarbons, etc.) and material eroded from internal surfaces
by various processes. The ability of the contaminants to
penetrate the core of the plasma, their ionization state and
their residence time in the plasma are also important factors
in determining their net affect on the plasma performance.

A number of techniques are being used to clean contaminants
from the plasma chamber. The most popular are the low pressure
hydrogen discharge[2] and the use of getters such as titanium.
Getters pose a potential problem in that they may absorb tritium
and increase the tritium inventory in the system.[3] Getters may
also deplete the plasma fuel by lowering the recycling rate.
The ability to clean the surface is an important consideration
in materials selection.

There are a number of erosion processes operational on a
surface in a fusion reactor environment.[4-7] These include uni-
polar arcing,[8] physical sputtering,[9] chemical sputtering,[10]
blistering[11] and vaporization. Unipolar arcing may occur on
surfaces which are cathodic to the plasma. Surfaces in contact
with a plasma will be negative with respect to the plasma
because of the higher mobility of the electrons compared to the
ions. The magnitude of this wall potential will depend on the
electron and ion temperatures at the edge of the plasma and is
about three times the electron temperature. In a tokamak reactor,
several hundred volts potential may be expected. In unipolar

arcing, a spot on the cathodic surface arcs to the plasma from which the current returns to the surface via a diffuse area. Unipolar arcs may initiate at foreign particles such as oxides and will move in the magnetic field. The arcing tends to vaporize the initiating spot as well as surface material along the arc track.

Typically, arc tracks seen in tokamak reactors, are 2-10 microns in depth and $10^{17}-10^{18}$ atoms/coulomb are eroded.[12] Unipolar arcs are in many ways similar to vacuum arcs which have been extensively studied.[13,14] Material eroded in vacuum arcs includes ions, neutral atoms and liquid droplets which may be ejected at high velocities (10^4 cm/sec).[15,16] It is generally thought that unipolar arcing in a tokamak reactor will decrease as the arc initiating spots are eroded away. Unipolar arcs seem to be most prevalent under unstable plasma conditions and in a tokamak reactor may be most evident at the beginning and end of the plasma discharge.[17] It is important to know the nature of the eroded material. If the eroded material is in the form of droplets, it may have a different impurity effect than if it is in the form of atoms or ions. Erosion by melting and droplet formation will probably eject more material than erosion by vaporization alone.

Physical sputtering[9] is a momentum transfer process in which bombarding particles create a collision cascade which intersects the surface giving enough energy to a surface atom to cause its ejection. The maximum energy (E) transferred by an incident particle to a lattice atom is given by:

$$E = E_i \frac{4M_i \, M_a}{(M_i + M_a)2} \qquad \text{Eq. 1}$$

Where E_i and M_i are the energy and mass of the incident particle and M_a is the mass of the lattice atom. The energy necessary to displace a lattice atom to an interstitial site is called the damage threshold and is typically around 25 eV for metals. The energy necessary to cause the ejection of a surface atom is called the sputtering threshold energy and is given by Eq. 1 where E_i would be the threshold energy and E is the surface binding energy of an atom. The sputtering yield is defined as the number of the atoms ejected per incident particle at a given energy. The sputtering yield and probably the sputtering threshold energy are functions of the angle of incidence of the bombarding particle with the maximum sputtering yield at 50-70° off-normal.

The theories of physical sputtering have been outlined by Sigmund[18] and Smith.[19] These theories do not account for the dependence of sputtering yield on bombarding particle dose[20] which is attributed to defect formation and the incorporation of bombarding particles in the near-surface region. Also the surface morphology which is developed by sputter erosion may affect the sputter yield.[21,22] This erosion morphology is determined by the metallurgical condition of the surface being eroded,[23] the presence of contaminants[24] and other factors. It should be noted that most of the reported sputtering yield studies do not specify the incremental or total ion dose, the metallurgical nature of the material being studied nor the initial

or final surface morphology. Mechanical texturing of surfaces has been shown to reduce sputtering yields by factors of 20-30[25] but also greatly increases the surface area which may pose contamination problems.

The effects of low energy ion bombardment on a surface are very complicated.[26] Backscattering, preferential sputtering, recoil implantation, reaction with gases in the system and selfsputtering may have important effects on surface composition. In the tokamak environment, the surfaces exposed to the plasma will be sputtered by low energy hydrogen bombardment (ion and neutral) contaminant ions, alpha particles, and ions of the eroded materials. The relative importance of these processes will depend on the plasma characteristics, contaminant levels and the surface materials.

Chemical sputtering may be regarded as enhanced sputtering due to chemical reaction of the bombarding species with the substrate material. This enhanced removal of material may be due to chemical reaction and volatilization by thermal agitation or by chemical reaction and physical sputtering of the new materials. In either case, one would expect that the temperature dependence of the sputtering process would be different from that using inert bombarding particles.[27] At very high temperatures, chemical sputtering decreases because of the decreased residence time of the reactive particles on the surface thus lowering the chemical reaction rates.

Blistering is exfoliation of surface material due to hardening and swelling of the near-surface material by radiation damage

and gas incorporation. Void formation[28] by defect and gas agglomeration weakens the material allowing easy fracture.[29] Hydrogen ion irradiation normally doesn't produce blisters on metals since the hydrogen atoms have a high mobility in the lattice.

Vaporization, of course, can occur when the materials are subjected to a thermal load such that the surface is vaporized. Therefore, it is desirable to use refractory materials where the thermal load can be high during normal operation or under fault conditions.

The hydrogen recycle properties of a surface are important to the operation of a fusion plasma since under sustained operations (>1 sec) the hydrogenic fuel particles will be re-cycled many times.[30] Both the recycle rate and the temperature of the recycled gas are of importance. A hydrogen particle incident on a surface can be reflected, physically or chemically absorbed on the surface and desorbed or become incorporated into the near-surface region and then desorbed.[31] Surface absorption will depend on the surface area. Hydrogen incorporation into the near-surface region will depend on chemical reaction, diffusion, solubility and chemical potential. It has been shown that the retention of low energy ions which will diffuse in the lattice of the near-surface region, is dependent on the defect concentration of the region since these defects act as trapping sites.[32,33,34] Tritium may also permeate the wall material.[35]

The mechanical properties of a material in a tokamak environment are of concern. Hydrogen and helium embrittlement,[29] sur-

face defects, radiation damage and the extreme thermal and mechanical environment may lead to premature mechanical failure of structural materials.

It should be noted that synergistic effects may be very important to the properties of the materials. Radiation damage (defects) may affect the recycling properties of a surface, gas incorporation, particularly helium, may affect the mechanical properties of a material. Contaminant gases may affect the arcing susceptability and so forth.

The properties of the materials used for the various components of a fusion reactor depend on the environment to which it is exposed, the performance desired and the effect of that component or material on the performance of the reactor. Coatings (or claddings) on internal components, vacuum walls, neutral beam injectors and divertors of fusion reactors may provide a desirable and possibly necessary engineering design flexibility to achieve controlled nuclear fusion.[36-40] In addition to the materials properties which have been discussed, a coating system imposes the additional requirement of coating-substrate adhesion which must be maintained under normal and fault operating conditions. Adhesion of a coating to a surface may be more related to fracture processes than to chemical bonding.[41] For this reason, the mechanical and thermal properties of the coating and substrate must be matched and such things as gas accumulation or eutectic formation at the interface must be avoided. Coatings (or cladding) on components should have thickness greater than 20 micrometers and may be formed by chemical vapor deposition (CVD), plasma enhanced CVD, plasma spraying, electroplating,

cementation processes, explosive cladding, glow discharge
reaction and many other techniques.

In addition to the relatively thick coatings normally
considered for components, it may be possible to form in-situ
coatings which are very thin but renewable by a variety of
techniques including: 1) deposition by plasma decomposition
of a compound,[42,43] 2) vapor deposition from a heated solid,[36]
3) solute segregation[44,45] or 4) redeposition of eroded material
as is now occurring in tokamak reactors.[46]

The properties of coatings and deposited materials are
often variable and sensitive to process and substrate variables.
Deposited materials often vary significantly from bulk material
as to grain size, defect concentration and other properties
dependent on atomic arrangement. Because of the diversity of
requirements on a coated surface in a fusion reactor and the
potential impacts on reactor performance, it is desirable to
have well characterized and reproducible coating materials for
study.

COATING PROPERTIES

Table 3 indicates the factors of importance in a fusion
environment and the properties of the coating which will affect
the material response. An asterisk (*) indicates the properties
and factors of immediate concern in the coating development for
limiters and wall armors. In some cases, the properties may
vary with exposure (erosion, radiation damage, etc.).

TABLE 3

COATING PROPERTIES

ADHESION*

Coating
    Thermal Conducitivity*
    Thermal Expansion Coefficient*
    Yield Stress
    Yield Strain
    Elastic Modulus
    Fracture Morphology*

Interface
    Hydrogen Trapping
    Void Formation
    Eutectic Formation
    Diffusion Coefficient*

Substrate
    Thermal Conductivity*
    Thermal Expansion Coefficient*
    Radiation Behavior (hν, n)
    Elastic Modulus

CONTAMINATION*

Coating
    Porosity/Surface Area*
    Absorption Characteristics*
    Desorption Characteristics*
    Surface Morphology
    Erosion Morphology
    Surface Reactivity

HYDROGEN RETENTION

Coating
    Permeation
    Solubility
    Thermal Desorption
    Compound Formation

Coating-Substrate
    Fracture Toughness

EROSION*

Arcing
    Electrical Conductivity
    Dielectric Phases
    Arcing Susceptability*
    Eroded Species*
    Erosion Morphology*

Blistering
    Void Formation
    Radiation Transmutation (n)
    Swelling
    Mechanical Properties

Physical Sputtering
    Grain Size
    Grain Orientation
    Surface Morphology
    Porosity
    Stoichiometry/Phase
        Distribution
    Sputter Yield* (Low and
        High Energy, Low and
        High Z, Dose, Angle)
    Erosion Morphology*

Chemical Sputtering
    Erosion Rates*

Vaporization
    Vapor Pressure
    Thermal Properties
    Emittance

GAS RECYCLING

Coating
    Trapping Defects
    Desorption Properties
    Reflection Properties

MECHANICAL PROPERTIES

Coating
    Surface Morphology
    Erosion Morphology
    Yield Stress
    Yield Strain
    Elastic Modulus
    Thermal Exp. Coef.
    Fracture Morphology

COATING CHARACTERIZATION

Characterization of a deposited material is essential to establishing reproducibility of the processing and of the material. The problem with characterization is that it presents an almost unlimited set of techniques and possibilities. Some properties can be determined with precision and accuracy, others may best be determined by response to testing.

The physical and chemical properties of the coating material can be determined by the conventional techniques of x-ray diffraction, scanning electron microscopy, transmission electron microscopy and diffraction, mercury porosimetry, metallography, electron microprobe, etc. Property determination of deposited materials is complicated by the growth morphology. Typically, deposited materials have a columnar growth morphology[47] when the ratio of the deposition temperatures, T, to the melting temperature, T_m, is less than about 0.4 (absolute temperatures).[48] The large columns (1-10 microns width) as seen in a fracture cross-section of these refractory materials consist of many small crystallites (0.01-0.1 microns) which are often equiaxed. The intercolumnar material is less dense than other material in the coating. This columnar morphology and extremely small grain size can make the deposited material behave in a very different manner from that of bulk material.

Adhesion is a major concern in any coating-substrate system. Though properties such as thermal expansion matching and inter-face structure may aid in deriving an adherent system in the final analysis testing is the most conclusive. The testing

program should be designed to reveal the fatigue properties
of the system. Pulsed electron beam irradiation is primarily
being used to test coating adhesion.[39] Thermal fatigue testing,
using multiple e-beam pulses of 2 kW/cm^2 for about one second,
has revealed several failure modes. Very poor adhesion is
revealed by coating spall. Poor adhesion is shown by coating
melt while good adhesion is shown by no failure on substrate
melt. In some cases, interfacial diffusion and reaction lead
to coating degradation and substrate melt. This latter mode
of failure may best be revealed by high temperature diffusion
studies.

Erosion of the coating material by arcing and sputtering
is of major concern. There is no absolute way to measure the
arcing properties of a material. Arc initiation seems to
depend on the presence of dielectric materials on the surface
which initiate the arc. Varying amounts of current are passed
through the arc. Without the dielectric material on the sur-
face, the arc will not initiate, hence arcing susceptability
is somewhat determined by surface contamination on conductors.
Using a system as described in Reference 49, arcing suscepta-
bility may be studied. Arcs which move over the surface are
observed and photographed and the resulting arc tracks can be
observed on the specimen surface. The amount of microarcing,
the rate of disappearance of the microarcs (clean-up) and
the observed arc tracks serve to give a relative arcing sus-
ceptability of the coating materials. The nature of the eroded
materials is determined by "catcher" experiments.

Erosion of the surfaces by physical sputtering in a
tokamak environment is probably very complicated since the
bombarding flux of hydrogenic species, their angle of incidence
distribution, contaminate particles and particles eroded from
surfaces is poorly defined and probably changes with time as
does the surface morphology, defect concentration and surface
composition. Accurate sputtering yield measurements must be
done on defined surfaces with known doses of mass and energy
analyzed bombarding particles at known angle of incidence, dose
rates and total doses. For most materials, an erosion morphology
will be generated on the sputtered surface and this morphology
may affect the sputtering yield, gas recycling and mechanical
properties. Little precise data has been published on the low
energy hydrogen ion sputtering yields of the materials of
interest as coatings. Comparative erosion yields may be made
using a Kaufman ion source which is not mass or energy
analyzed.[39,50] These erosion data are not true sputtering
yields but are useful in making comparisons.

In addition to the sputtering yield and erpsion morphology
of surfaces under low energy hydrogen ion bombardment, the
sputtering yield of and erosion morphology generated by high
energy hydrogen ions and by higher Z particles should be
determined. In some instances, very unusual surface morphologies
can be generated on ion eroded surfaces.[21] It is expected that
the stoichiometry, phase distribution, grain size, grain orien-
tation, surface morphology, porosity, angle of incidence of the
bombarding particles and other factors will affect erosion yield
measurements.

Chemical erosion of the coating materials should be determined as a function of temperature. Stoichiometry, phase distribution, grain size, grain orientation, surface areas and other such factors will influence the erosion rate of materials subject to chemical erosion. Chemical erosion depends on chemical reaction of the reactive plasma or ions and the removal of the surface species by sputtering and/or vaporization. To completely characterize this process would be very complicated since the plasma temperature, surface fluxes, surface composition, erosion species, etc. would have to be known. At present, it seems that the best that can be done is to determine the relative chemical erosion rates in a constant environment being careful that the surface is not contaminated by materials from other eroded surfaces.

The potential for contamination due to outgassing and desorption is directly related to the porosity and surface area of the deposited material. Perhaps under continued use a porous material will clean up but the porosity and surface area will continue to affect gas recycling. Porosity can be determined by mercury and helium porosimetry and surface areas can be determined by gas absorption techniques.

Gas recycling will be dependent on the surface area and its availability to bombarding plasma species as well as reflection, adsorption/desorption and trapping defects in the near-surface region. Generally, very sophisticated techniques have to be used to characterize the defect properties of a material without introducing more defects.[32,33,34]

Mechanical and thermal properties of the coating substrate systems need to be determined in order to make a computer analysis of the thermal and stress profile seen by the materials. Both the mechanical and thermal properties will be greatly affected by the porosity, morphology, preferred orientation and composition of the coating materials.

COATING-SUBSTRATE SYSTEMS

In developing coatings for specialized environments, one must determine whether or not one material is so much better than others that the coating material should control the development. If not, the development may be controlled by the availability of processing, desirable substrate properties, the potential for scale-up, etc. To make this determination, screening tests may be used to determine relative properties such as adhesion, arcing susceptability, chemical erosion, and sputter erosion. Coating materials with good adhesion properties, low erosion rates, low Z and high temperature stability are desirable. For low temperature, actively cooled components, coatings of nonrefractory materials may be of interst.

Several coating/substrate systems have been studied and are under development for fusion reactor applications. These include TiB_2 on POCO graphite and molybdenum by CVD,[39,50-56] TiB_2 on copper and stainless steel by plasma spraying,[39,49,50] B_4C (+B) on POCO graphite by CVD,[39,50,57] SiC by sputter deposition,[58] B on POCO graphite by CVD,[39,50,59] Be by vacuum evaporation,[21,39,50] Be on copper and stainless steel by plasma

spraying,[39,49,50] VBe_{12} on copper and stainless steel by plasma spraying,[39,49,50] and carbon by vacuum evaporation.[60,61,62]

At the present time, the materials of most interest are TiB_2, B, B_4C and TiC on graphite for limiter and armor applications. The titanium compounds may pose a problem if they decompose on erosion to elemental titanium which will absorb the hydrogenic species.

Transmutation of the[10] B isotope under neutron irradiation may pose a problem when using the naturally occurring boron (80%[11] B, 20%[10] B). Calculation of the transmutation of naturally occurring boron on the first wall surface by the neutron spectrum in the UWMAK III show a depletion of about 2%/MW-Yr.* Pure[11] B material can be prepared by using isotopically separated materials in preparing the deposition materials.

SUMMARY

Coatings of fusion reactor components may provide a needed design flexibility to achieve controlled fusion reaction. The stringent requirements on coating systems impose a real challenge for the development of coatings for these applications. Coating development has just begun and the need and desirability of coatings will probably increase as the reactor environment becomes more severe.

*Calculations by G. L. Kulcinski, Univ. of Wisconsin.

ACKNOWLEDGEMENTS

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TABLE 1

TYPICAL OPERATING AND FAULT ENVIRONMENTS

MODERATE SIZE (EPR) FUSION REACTOR

		First Wall	Neutral Beam Injector Armor	Limiter
Normal **Operation** **(200 MJ Plasma)**	Fast Neutrons >13 MeV	$5\text{-}10 \times 10^{13}$ cm^{-2}/s	$5\text{-}10 \times 10^{13}$ cm^{-2}/s	$5\text{-}10 \times 10^{13}$ cm^{-2}/s
	Total Neutrons	$1\text{-}5 \times 10^{14}$ cm^{-2}/s	$1\text{-}5 \times 10^{14}$ cm^{-2}/s	$1\text{-}5 \times 10^{14}$ cm^{-2}/s
	D, T, He	$5\text{-}10 \times 10^{15}$ cm^{-2}/s ($\overline{T} = 0.2 - 3$ KeV)	Shinethrough $10^{16} - 10^{18}$ cm^{-2}/s ($\overline{T} = 60 - 200$ KeV D^0)	$10^{18} - 10^{19}$ cm^{-2}/s ($\overline{T} = 0.2 - 3$ KeV)
	e^-	----	----	$10^{18} - 10^{19}$ cm^{-2}/s ($\overline{T} = 0.2 - 3$ KeV)
	Radiation	$10^{-2} - 10^{-3}$ Kw/cm^2	$10^{-2} - 10^{-3}$ Kw/cm^2	$10^{-2} - 10^{-3}$ Kw/cm^2
	Total Thermal Load	0.01 - 0.5 Kw/cm^2	0.05 - 1 Kw/cm^2	0.5 - 5 Kw/cm^2
	Unipolar Arcing	?	?	?
Fault Conditions **1. Plasma Dump in 10-100μs**	D, T, e^-	$10^{19} - 10^{21}$ cm^{-2}/s ($\overline{T} = 5\text{-}10$ KeV)	$5\text{-}50 \times 10^{17}$ cm^{-2}/s (D^0)* ($\overline{T} = 60\text{-}200$ KeV)	Same as Wall
	Thermal Load	$10^4 - 10^6$ Kw/cm^2 (Local - 1/3 Wall)	5-10 Kw/cm^2 (D^0)*	Worse than Wall
2. Runaway Electrons	e^-			$10^{18} - 10^{19}$ cm^{-2}/s >1 MeV

*With no plasma, the neutral beams will strike the armor for 0.1 sec. If the plasma dumps onto the armor, these values would be in addition to the first wall parameters.

TABLE 2

ENVIRONMENTAL EFFECTS

Environment	Wall	Wall Armor	Limiter
Neutron Bombardment	Void Formation, Sputtering	Void Formation, Sputtering	-------
D, T, He Bombardment 0.2 - 3 KeV	Sputtering, Chemical Erosion Losses, Recycling	Sputtering, Chemical Erosion Losses, Recycling	-------
D^o Bombardment 60-200 KeV	--------	Implantation, Blistering, Displacement Damage	-------
Thermal Load	Heating, Vaporization	Heating, Vaporization	Heating, Vaporization (No Cooling)
Thermal Pulse	Shock, Fatigue	Shock, Fatigue	Shock, Fatigue
Unipolar Arcing	Vaporization, Surface Melting	Vaporization, Surface Melting	Vaporization, Surface Melting
Plasma Dump	Vaporization, Mechanical Stress	Vaporization	Vaporization

NEUTRAL BEAM
INJECTOR

WALL
ARMOR

LIMITER

PLASMA

LIMITER

1st WALL
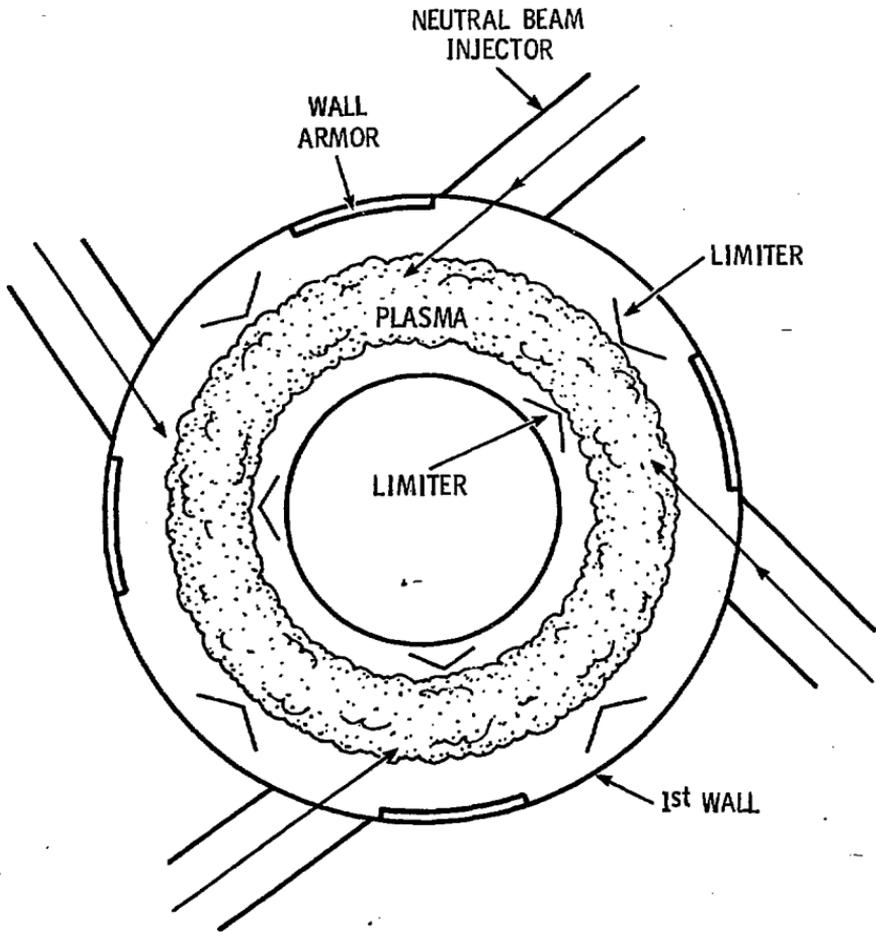
SCHEMATIC OF TOKAMAK REACTOR

Figure 1: Idealized schematic of tokamak fusion reactor.

Figure 1:   Idealized schematic of tokamak fusion reactor.