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APPLICATION OF THICK FILM AND BULK COATING TECHNOLOGY TO THE SUBTERRENE PROGRAM*

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ABSTRACT

The Subterrene is a rock-melting earth-penetration system representing a significant advancement in excavation technology. Temperatures of 1700-2000 K are involved, and heated refractory-metal or alloy probes are used. Corrosion problems are severe on the exterior surfaces of the refractory metals used; bulk coatings having the required properties would be extremely desirable provided, they could be deposited upon a substrate as a tenacious coating.

Within the Subterrene pyrographite radiant heaters are operating at temperatures to 2450 K. Graphite receptors added to improve the radiant heat transfer react with the molybdenum and tungsten penetrator bodies to form the respective carbides. A 30 μm-thick CVD film of TaC may be applied to inhibit this reaction.

The techniques of applying these films, their nature, and the results of their application, are discussed. The environment of an operating penetrator is described, and the requirements and properties of exterior coatings are outlined.

*Work done under the auspices of the U. S. Atomic Energy Commission and National Science Foundation-Research Applied to National Needs (RANN).

I. Introduction

The Subterrene is an earth-penetration system, which promises to lead to significant advances in excavation technology. Operating essentially by rock-melting, the Subterrene accomplishes simultaneously three aspects of excavation, namely: penetration, casing formation, and debris removal. The casing, or liner, consists of solidified rock melt; the debris is removed either by extrusion of the chilled melt to the surface, or by consolidation, a method which takes advantage of a suitable difference between the densities of the solid rock and the rock melt thereby allowing all of the rock glass to remain in the bore as a casing. Four types of Subterrene penetrators are shown in Fig. 1 which also illustrates some points mentioned above concerning liner formation and debris removal.

Projected uses of the Subterrene concept encompass a wide variety of projects and range from utility-line emplacement to deep drilling into hot rock for geothermal-energy extraction to large-scale transportation tunneling. In the latter case, a nuclear reactor is envisaged as the heat source and heat pipes will be used as thermal conductors to bore and line tunnels up to 10 m in diameter.

While in some cases penetration rates of the Subterrene compare favorably with those of conventional drilling and tunneling techniques, and can occasionally even exceed conventional rates (e.g., in deep, hot-rock drilling), we must in general, consider the entire excavation process including liner formation and debris removal to appreciate the economic advantages of the Subterrene. Further details of all aspects of the Subterrene concept are available in the open literature.[1]

Many common rock materials melt between 1350-1700 K, and Subterrene surface temperatures are necessarily this high or slightly higher, while Subterrene interior temperatures may be as high as 2450 K. These elevated temperatures create and intensify the corrosion conditions which we are attempting to understand and control. Figure 2 illustrates a consolidating penetrator in cross section, and serves as a reference for the discussion that follows. An insulator of oriented pyrographite at the aft end of the penetrator tip isolates the tip thermally from the trailing stem. The stack of graphite disks inside forms a radiant heater that operates typically at 4-10 kW ($\sim$ 1-4 MW/m^2 at the heater surface) and a temperature of $\sim$ 2450 K. A graphite receptor on the inner surface of the metal penetrator body improves the transfer of radiative power to the body by matching the emissivities of the radiant heater and the penetrator body. Penetration is effected by forcing the hot tip through the rock.

Chemical reactions pose problems at the interfaces between the metal and the carbon, and at the outer surface of the penetrator. Carbiding reaction between the receptor carbon and the metal body results in a metal-carbide layer (Mo_2C, in the case of a molybdenum penetrator body) that can cause failure of the unit. Externally, there are corrosion reactions between the metal penetrator body and some rock-melt components such as oxygen or iron. It is for these two areas that we have considered the application of thick films or bulk coatings as reaction inhibitors.

II. Tantalum Carbide-Coated Receptor

The penetrator bodies of present Subterrene prototypes are made from molybdenum and tungsten. The reaction at the interface between the receptor and the metal penetrator body is now fairly well understood in terms of carbon diffusion through the metal-carbide layer that forms at the interface. Using the rate data of Fries, et al,[2] we can calculate the extent of carbide formation and obtain results that are in agreement with measurements on prototype molybdenum penetrators.[3] Theoretical lifetimes of such penetrators for systems of interest are of the order of 1 Ms (~ 275 h) until the time the receptor is completely lost;[4] typically, however, failure occurs earlier because of buckling and/or shorting of the Mo_2C layer.

Carbon diffusion in tantalum carbide has been studied extensively elsewhere.[5] Extrapolation of results suggests that a thin coating of TaC on the outer surface of the receptor would serve as an effective diffusion barrier. (The ratio of the diffusion coefficients of carbon in Mo_2C and TaC is about 2350 at a temperature of 1900 K.)

We have applied 30 μm-thick coatings of TaC onto the graphite receptor in a chemical vapor-deposition process. The deposition process, discussed in detail elsewhere,[6] is expressed for TaC by the following equation:

$$TaCl_5(g) + 5/2\ H_2(g) + x[C] = TaC_x + 5HCl(g). \qquad (1)$$

The brackets on the carbon symbolize the fact that we are dealing with a surface having a carbon activity, a_c, < 1. In effect, tantalum is being deposited on a surface where it reacts with carbon that has diffused

from the receptor substrate. Obviously, a carbon activity gradient must exist across the carbide layer if carbon is to diffuse. Furthermore, the activity of the carbon at the fresh surface also controls the deposition rate of tantalum by shifting the free energy of reaction, ΔG_r, for reaction (1) from negative values (high a_c) to positive ones (low a_c). If the pressures of the hydrogen and hydrogen-chloride gases in the system are set and held constant during a deposition, the quotient $p^5_{HCl}/p^{5/2}_{H_2}$ is also constant, with the end result that the thickness of the deposited layer is controlled rather closely. For given deposition conditions, for example, an area that is relatively thin in comparison to the adjacent TaC film will have a higher carbon activity at the surface. Then, reaction will occur more readily at this area, thus building up the film thickness more rapidly. The converse, i.e., that thicker areas will build up more slowly, is obvious.

A schematic of the coating system and associated gas-flow lines is shown in Fig. 3. The $TaCl_5$, a powder at room temperature, is fed directly into the preheated manifold gases as a fluidized powder that is flash-vaporized on entering the reaction crucible. All inlet and outlet manifold lines connected to the crucible are electrically heated to prevent condensation and blockage by the $TaCl_5$. The valving and flowmeters on the inlet side allow control of the reactants; the trap and scrubber on the outlet ensure removal of particulates and of HCl from the exhaust gases. The inductively heated graphite crucible has an inner diameter of $\sim$ 230 mm and is 440 mm deep. Typical operating conditions during coating of the receptors are shown in Table I.

TABLE I

PROCESS PARAMETERS FOR TANTALUM CARBIDE DEPOSITION

Temperature, K	2273
Argon flow rate, 10^{-5} m^3/s*	40.0
Hydrogen flow rate, 10^{-5} m^3/s*	1.7
Hydrogen Chloride, 10^{-5} m^3/s*	6.7
$TaCl_5$ flow rate, mg/s	126

*Flow is measured at STP.

Under these conditions a 30 μm-thick TaC film was deposited uniformly on the outer surface of the receptor in 4.5 ks (∿ 1.5 h). The receptors have an outside diameter of ∿ 18.6 mm and are 70 mm long, with a surface area of ∿ 4000 mm^2. A certain amount of fixturing or sample-mounting was required to allow the outer surface and the ends of the cylindrical shell to be coated, but not the interior.

The yellow-gold color of the coating indicated a highly stoichiometric carbide, ∿ $TaC_{0.98}$. The outside diameter of the receptor increased only nominally, in many cases by not more than 50% of the coating thickness, because of partial inward growth into the receptor wall. Figure 4 shows some photomicrographs made through a scanning-electron microscope (SEM). A network of small (∿ 1-2 μm) carbide crystals interlocking with the graphite structure is clearly discernible. Moving outward from this interface, by about one third of the film thickness, the TaC crystals somewhat abruptly become much larger, by a factor of five to six. A generally columnar structure for these larger crystals is suggested.

Microscopic examination revealed little carbon concentration in grain boundaries; it may therefore be concluded that bulk diffusion is the predominant transport mechanism at the temperatures of deposition.

Two TaC-coated POCO-graphite receptors have been put to test in laboratory systems that are similar to consolidating penetrators. The first receptor operated at a heater temperature of 2450 K for 0.72 Ms (∿ 200 h) before removal from test. The temperature or the surface of the test penetrator was measured to be 1800 K. The Mo_2C layer that had formed showed a thickness of 0.076 - 0.152 mm, with the higher

value suspect as too large because of temperature inhomogeneity.[7] Assuming a uniform temperature of 1800 K and no TaC barrier, a Mo_2C layer ∿ 1.3 mm thick can be expected in a 720-ks period. Calculating the thickness if a TaC barrier is present is more complex, but some simple estimates yield 0.25 mm as a maximum.

The test data for the second unit, although not yet completely analyzed, appear to confirm the above results. In this experiment the heater operated at the lower temperature of ∿ 2370 K for 1.0 Ms (∿ 278 h). The receptor remained intact and in good condition, with no buckling, shorting, or excessive Mo_2C formation. It will be recalled that this test time is equivalent to the theoretical lifetime of an unprotected receptor. The results strongly suggest that a thin TaC layer can be deposited uniformly and to function effectively as a carbon-diffusion barrier at temperatures of ∿ 1800 K.

III. Exterior Corrosion

As indicated above, we are investigating the use of molybdenum and tungsten as penetrator-body material. It is not yet clear whether these metals are best for Subterrenes. The high-temperature strength properties of these materials are an obvious advantage. However, reaction (in some cases severe) has been observed for penetrators in contact with basalt or tuff rock melts. Corrosion conditions are severe on the exterior surfaces, due to:(1) the high temperatures, (2) the reactive species present in the molten rock glasses, and (3) the abrasive effect of undissolved or unmelted particles in the glass.

While the corrosion reactions are not yet clearly understood, evidence indicates at least two mechanisms. One involves a gas-phase reaction between the metal and the rock-melt constituents, whereas the other might be termed a dissolution of the metal in the rock melt. Intergranular attack is observed in the latter case; in some cases of fast-grain growth at elevated temperatures, deterioration is noted when the large grains split off from the main body.

Neither molybdenum nor tungsten is immune to these corrosive effects, although their lifetimes might be acceptable. We continue to investigate refractory alloys of suitable high-temperature strength and hardness; grain-growth-stabilized materials such as thoriated tungsten are being examined. However, the inertness of some borides, carbides, nitrides, and silicides suggests their possible use either as penetrator-body materials or as coatings. Suitable coatings must have a mix of desirable properties: a high melting (or decomposition) point, high strength and hardness at high temperatures, good thermal conductivity, resistance to corrosion (particularly to oxidation) and a coefficient of thermal expansion (CTE) close to that of the substrate material.

Properties of prospective coating materials are listed in Table II, along with comparable data for molybdenum and tungsten. In terms of matching the coefficients of thermal expansion to those of a molybdenum or tungsten substrate, and at the same time maximizing the thermal conductivity, hardness, and decomposition temperature, several promising materials present themselves, e.g., HfB_2, many of the cartides, and WSi_2. However, the one unknown factor remains their reactivity with rock melts. Our investigations indicate that, for example, WSi_2 is rapidly attacked

by molten basalt; but that ZrB_2 is more resistant. Until these compatibilities are determined more thoroughly we are unable to recommend a specific coating. Finally, given a coating material with suitable physical and chemical properties, we still must develop a method for applying this material to the penetrator surface in a uniform, well-bonded layer.

IV. Summary

We have considered the application of thick protective films to components used in the Subterrene rock-melting program. A 30 μm thick TaC coating has been chemically vapor-deposited, with good results, on an inner graphite radiant heater receptor to inhibit carbon diffusion into the metal of the penetrator body. Refractory metal borides, carbides, and silicides are suggested as coating materials to minimize corrosion on the exterior surface of the Subterrene penetrators. However, resistance of these materials to corrosive attack by rock melts remains to be studied more fully, and techniques for applying these coatings must be developed.

V. Ackrowledgements

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TABLE II
SELECTED PROPERTIES OF PROSPECTIVE SUBTERRENE PENETRATOR COATING MATERIALS

Compound	T_M (or T_D), K	Microhardness Kg/mm^2	@ T,K*	Thermal Conductivity W/mK	@ T,K*	Coefficient of Thermal Expansion $10^{-6}K^{-1}$
Mo	2883	~240 ~160	800 1700	76	2000	5-8
W	3683	~480 390	800 1700	107	2000	4.4-5.8
TiB_2	~2873	2710	--	4.2	1700	8.1
ZrB_2	3260	1560	--	25	500	6.9
HfB_2	3523	2900	--	--	--	5.7
Mo_2B	2273	--	--	--	--	--
MoB	2453	2350	--	--	--	--
W_2B	2310	--	--	--	--	--
WB	3193	3700	--	--	--	--
TiC	3340	500 2900	1100 300	45	2000	7.7
ZrC	3693	2600	--	44	2373	6.7
HfC	4201	2700	--	29	273	6.6
VC	2921	2900	--	39	273	7.2
NbC	3873	2400	--	18	273	6.6
TaC	4256	2500	--	22	--	6.3
W_2C	3023	3000	--	20	1073	5.8
WC	3049	2100	--	196	--	4.2-5.0
SiC	2973	3350	--	46	1273	5.7
TiN	3222	2000	--	6	1223	9.4
ZrN	3255	1500	--	5.4	1073	7.2
HfN	3660	1600	--	21.8	--	6.9
VN	2450	1500	--	11.3	--	8.1
NbN	2477	1400	--	3.8	--	10.1
TaN	3366	1000	--	8.5	--	3.6

TABLE II

(Continued)

Compound	T_M (or T_D), K	Microhardness Kg/mm^2 @ T,K*		Thermal Conductivity W/mK @ T,K*		Coefficient of Thermal Expansion $10^{-6}K^{-1}$
Si_3N_4	>2173	1100	--	17.2	--	2.8
AlN	2773 (Sub)	1130	--	20	1073	6.1
Al_2O_3	2288	~2000	--	5.8	1250	8.0
BeO	2823	~2000	--	18.7	1250	9.5
ZrO_2 (stabilized)	2873	~ 800	--	2.3	1250	5.5
$MoSi_2$	~2250	1259	--	~38	811	9.2
WSi_2	2433	1090	--	48	--	6.3-7.9

*No entry in the temperature column signifies data taken at or near room temperature.

Figure Captions:

Fig. 1. Schematic diagram of penetrator melting modes and melt handling methods.

Fig. 2. Consolidation penetrator cross-section.

Fig. 3. Gas flow diagram of coating system.

Fig. 4. Scanning electron photomicrographs of fractured TaC-coated graphite receptor. Dark area is POCO graphite substrate, light-colored material is the TaC coating.

a) 1000x

b) 2000x

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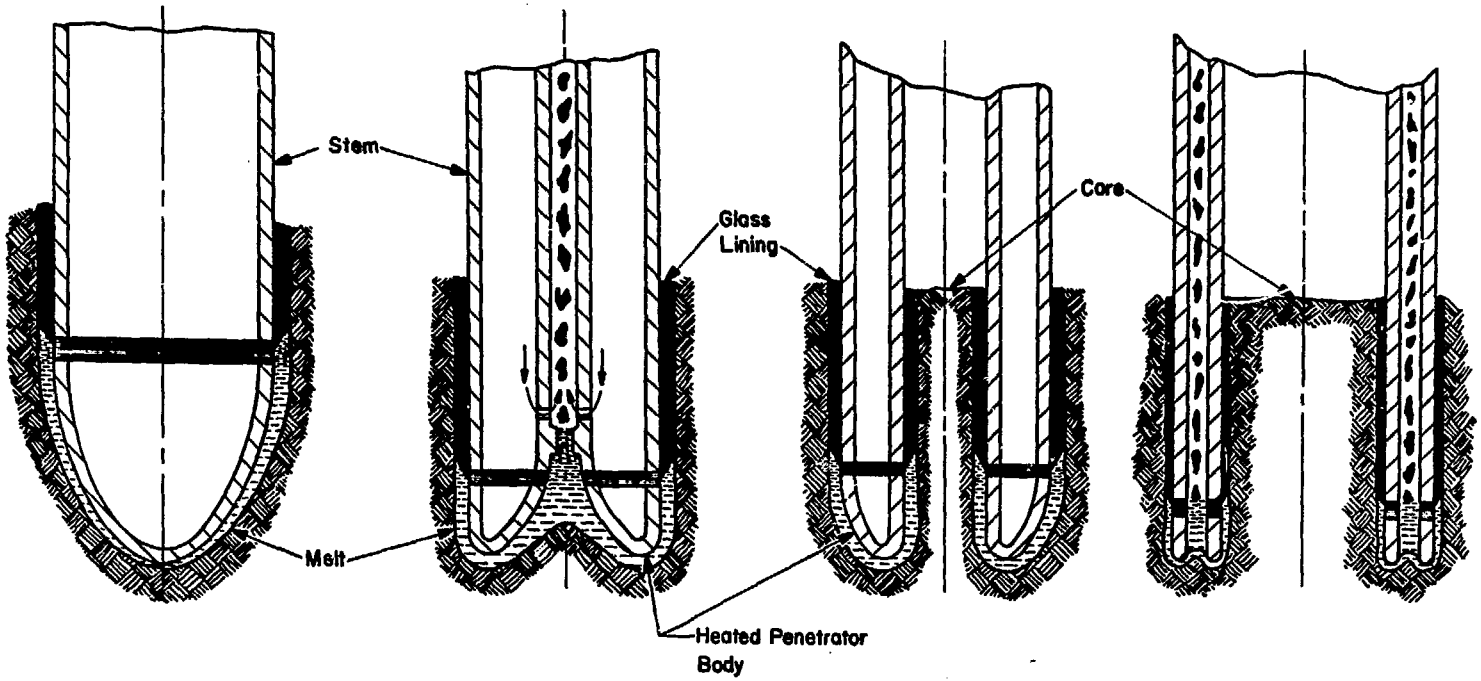
Stem
Glass Lining
Core
Melt
Heated Penetrator Body
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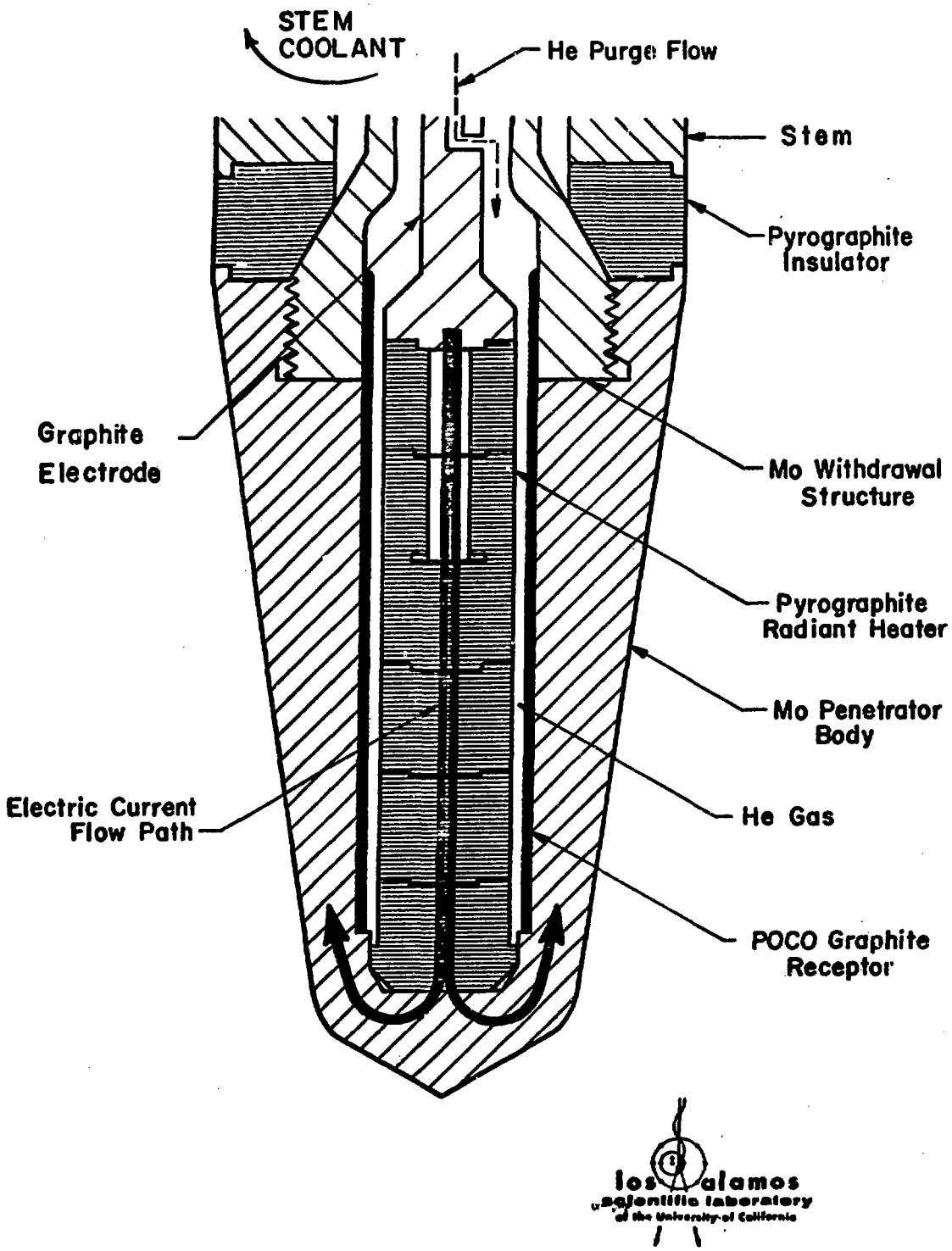
(b) Extrusion
(c) Coring With Consolidation
(d) Coring With Extrusion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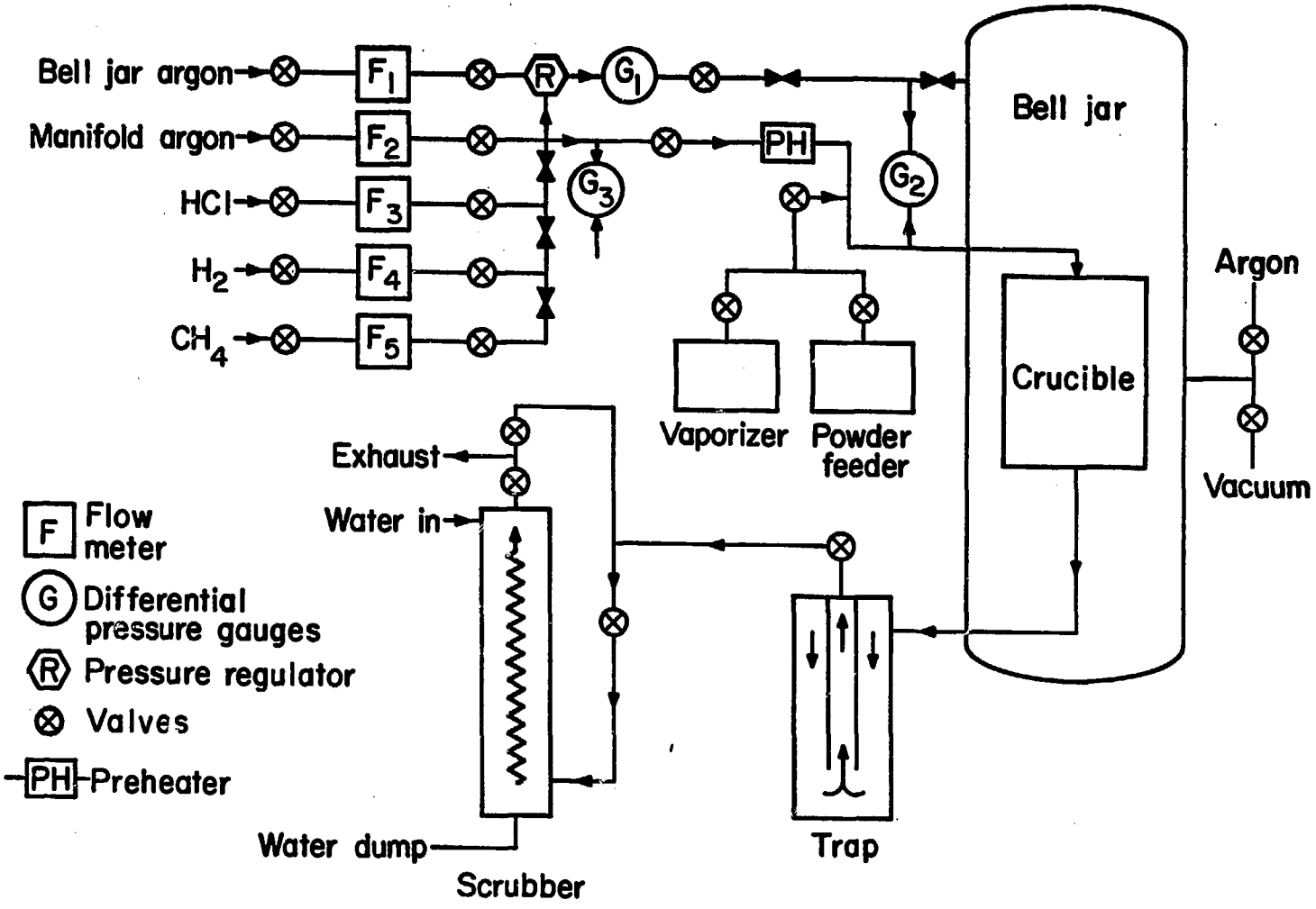
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Manifold argon
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G_3
PH
Bell jar
Argon
Crucible
Vacuum
Vaporizer
Powder feeder
Exhaust
Water in
Water dump
Scrubber
Trap
F Flow meter
G Differential pressure gauges
R Pressure regulator
Valves
PH Preheater