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SNAP FUEL ELEMENT CLADDING (U)

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GENERAL ATOMIC
DIVISION OF
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**PROPOSAL FOR DEVELOPMENT OF
SNAP FUEL ELEMENT CLADDING (U)**

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I. INTRODUCTION

The present design of the SNAP-8 fuel element is based on a zirconium-uranium alloy, hydrided to an H/Zr ratio of 1.7. The elements are about 5/8 in. in diameter and 16 in. long. The fuel rod is encapsulated in a Hastelloy N cladding with a 10 mil wall. The interior surface of the cladding is coated with 3.5 mils of a barium silicate glass for the purpose of hydrogen retention. (Details of the fuel element specifications are given in Table I). The glass coating, if intact, provides a sufficient barrier such that the hydrogen loss, at least for the current generation of SNAP-8 reactors, is kept within the specified limits.

It is our understanding that among the current items of concern regarding the SNAP-8 fuel are:

1. Cracking of the glass coating at ambient temperatures during the launch vibration, with subsequent increased loss of hydrogen.
2. Swelling of the hydride fuel element under irradiation. Current experiments seem to indicate swelling of about 6 volume percent per atomic percent burnup of the fuel.

Recent conversations⁽¹⁾ with personnel of Atomics International, the prime contractor for SNAP-8, have indicated that present coatings, at operating temperature, are considered to be adequate for the first generation of SNAP-8 reactors, but that improved methods of hydrogen retention must be developed for the more advanced systems of the future. Less optimism was expressed about the problem of fuel swelling, however. The problem of fuel swelling is independent of the cladding material and is not considered in this proposal.

During the past several months General Atomic has carried out a number of preliminary investigations which indicate that it may be possible to attain low hydrogen permeation rates by utilizing recently developed vapor deposition techniques to deposit claddings of refractory metals on the fuel

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Table I

SNAP-8 FUEL ELEMENT SPECIFICATIONS

Number of elements per core	211
Fuel element material	(10U-90Zr)H _{1.7}
Fuel rod diameter, in.	0.529
Fuel rod length, in.	16.0
Cladding thickness, in.	0.010
Cladding OD, in.	0.560
Ceramic hydrogen retention coating, in.	0.0035
Cladding material	Hastelloy N
Degree of hydriding, $N_H \times 10^{22}$ atoms/cc (core average)	6.0 ± 0.1
Hydrogen/zirconium ratio	1.7
Uranium content of fuel alloy, percent	10.00 ± 0.13
Uranium enrichment, wt-% U ²³⁵	93.15 ± 0.10
Fuel burnup, metal atom-% (fissions per total metal atoms)	0.32
Hydrogen permeation, percent in 10 ⁴ hours operation	5
Clearance between fuel element and ceramic coating, in.	0.002

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rod. The possible application of layer-type claddings with markedly lower permeation rates has also been deemed possible. In addition, the literature indicates that these materials have adequate resistance to NaK in the temperature range of interest.

General Atomic, in this proposal, outlines a 12-month initial program of research and development directed toward the development of a fuel element which can be utilized in the SNAP-2, 10A, and SNAP-8 class of reactors and, indeed, in other compact, high-power-density reactors. Basically, the present purpose is to develop a structurally sound metallic cladding for the zirconium-uranium hydride rods which serve as fuel elements for SNAP-type reactors. The goal is to develop a cladding which, as a hydrogen barrier, will be significantly more effective at elevated temperatures than current coatings and which will have, at ambient temperatures, the strength to withstand the vibration and acceleration forces at launch without cracking. It is recognized, however, that the specific work proposed herein is of a preliminary nature and promising results in the research outlined in this proposal would have to be obtained before the direction of a future program could be determined.

The research and development program outlined below is divided into four parts (Sections II-V). Section II briefly outlines the present knowledge of the hydrogen permeation of metals and describes the various studies on this problem General Atomic proposes to undertake under this program. Section III is concerned with the compatibility of the cladding material with both the NaK and the zirconium hydride fuel. Section IV deals with the study and development of the coating process and the investigations of the effect of the variables in the coating process on the hydrogen permeation rate. Section V discusses the relatively small program in nuclear physics proposed, whose purpose is to determine the effect of the various claddings on the neutronic behavior of the reactors.

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Section VI, in providing a statement-of-work suggested for use in any contract authorizing the proposed work, serves as a summary of the technical program. This is followed by a section describing briefly the qualifications and experience of key personnel expected to participate, and the last section sets forth an estimate of the costs of the program.

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II. HYDROGEN RETENTION STUDIES

2.1. BACKGROUND AND THEORY

The permeation of hydrogen through metals has been studied rather extensively in recent years. Flint⁽²⁾ studied and comprehensively reviewed the diffusion of hydrogen through materials of construction, principally the steels, and Klapp and Barth⁽³⁾ in 1960 reviewed the diffusion of interstitials in refractory metals. In addition, there have been numerous studies of the permeation of pure metals by hydrogen.

This discussion is concerned with the process by which hydrogen permeates a metal. This process involves the adsorption of hydrogen on the surface of the metal, the solid state diffusion of hydrogen through the metal lattice, and the desorption of hydrogen from the other side of the barrier. The permeation process is dependent both on the rate of diffusion of the interstitial through the lattice of the metal and on the solubility of the interstitial in the metal. Indeed, if a gas is not soluble in a metal it will not diffuse (or permeate) through the metal. Thus, either a low solubility or a low diffusion rate leads to a low permeation rate.

While present knowledge of the diffusion process is incomplete, it has been shown in several cases^(4, 5) that the diffusion of hydrogen through a number of metals takes place by a lattice diffusion process rather than along the grain boundaries. That the diffusion of hydrogen through metals takes place in the atomic state is evidenced by the dependence of the rate on the square root of the pressure. If the rate-controlling process in the permeation of the gas through the metal is the diffusion of the atoms of the gas through the lattice of the metal, then the permeation rate can be related to the diffusion rate by the equation

$$P[\text{cm}^3(\text{STP})\text{-cm/cm}^2\text{-sec}] = D \times S, \quad (1)$$

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where D is the diffusion coefficient in cm^2/sec at temperature T , and S is the solubility in standard cm^3 per cm^3 of metal at a given temperature T at 1 atm pressure. The permeability represents the amount of gas, in standard (STP) cm^3 , which passes in one sec through a cross section 1 cm^2 in area and 1 cm thick.

In the absence of the formation of a hydride phase, the solubility, S , of a diatomic gas in a metal has been found to be given by the equation

$$S = k p^{1/2}, \quad (2)$$

where k is the solubility (Sievert's law) constant and p is the pressure in atm. It is clear that for the gas to diffuse through the solid metal (lattice diffusion) and not through the pores or cracks, the gas must be soluble in the metal.

The diffusion of gases through ^{some} metals has been studied less well, especially in the case of the refractory metals. The equation which governs the temperature dependence of the diffusion process is

$$D = D_0 e^{-\Delta H_d / RT}, \quad (3)$$

where D_0 is the diffusion constant in cm^2/sec ,

ΔH_d is the activation energy in kcal/mole, for the diffusion process

R is the gas constant, and

T is the absolute temperature.

Similarly, the temperature dependence of the solubility may be represented by

$$S = S_0 e^{-\Delta H_s / RT}, \quad (4)$$

where S_0 is a constant in cm^3 (STP) of gas/ cm^3 of metal, and ΔH_s is the heat of solution.

Combining Equations 1, 3, and 4 we obtain

$$P = D_o S_o e^{-(\Delta H_d + \Delta H_s)/RT} \quad (5)$$

or

$$P = P_o e^{-\Delta H_p/RT}, \quad (6)$$

where $P_o = D_o S_o$, and $\Delta H_p = \Delta H_d + \Delta H_s$ is the activation energy for the entire permeation process. From the permeation experiments to be described in this proposal the quantity ΔH_p can be determined. Separation of this constant into the activation energy for the diffusion process and the heat of solution requires a determination of either (1) the solubility of hydrogen in the metal as a function of temperature so that ΔH_s may be evaluated or (2) the diffusion coefficient as a function of temperature. Thus, to gain this valuable information, as an ancillary experiment in the proposed program an attempt will be made to measure the solubility of hydrogen in the metals to be used as cladding materials.

For a specific permeation barrier of area A and thickness L, through which hydrogen has been flowing for t seconds with a hydrogen pressure of p_1 atm on the inlet side and p_2 atm on the outlet side,, the quantity of gas, α , in cm^3 (STP) which has permeated the barrier may be written as

$$\alpha = \frac{S_o D_o A t}{L} \left(p_1^{1/2} - p_2^{1/2} \right) e^{-\Delta H_p/RT}, \quad (7)$$

where A is the area in cm^2 ,

t is the time in sec, and

L is the barrier thickness in mm.

In many experiments, the outlet pressure of the diffusing gas is kept at zero either by the maintenance of a vacuum on the outlet side or by sweeping the outlet side of the barrier with an inert gas. In these cases $p_2 = 0$. For a given barrier, in which A and L are constant, Equation 7

may be rewritten as

$$R = \frac{\alpha L}{At p_1^{1/2}} = S_o D_o e^{-\Delta H_p / RT}, \quad (8)$$

where R is the specific permeation rate in $\text{cm}^3(\text{STP})\text{-mm}/\text{cm}^2\text{-sec-atm}^{1/2}$.*

The experimental difficulties involved in the measurement of permeation rates have been discussed by Flint.⁽²⁾ Two methods are generally used, the disc and tube techniques. Briefly, the disc technique involves the measurement of the permeation rate through a thin flat disc of barrier material sealed between an inlet and an outlet tube. In this method the problem of sealing the disc between the walls of the tube is predominant. In the tube technique a cylindrical tube, closed on one end, is used as the barrier. This method presents the problems of joining the diffusion-barrier tube to a sampling tube of lower permeability and the measurement of the correct diffusion area since some part of the tube must be in the zone of a temperature gradient.

For some of the materials to be investigated in this work, the tube technique presents fewer problems. Therefore, except for the single crystal studies described later, it is adopted as the proposed method of measurement.

A schematic diagram of the proposed permeation apparatus, utilizing the tube technique, is shown in Figure 1. The sample is contained in an inconel tube and held at constant temperature. A slow stream of argon flows inside the tube and sweeps the released hydrogen through the sample collection bulb of the gas chromatograph. A sample of the effluent gas is trapped periodically and injected into the chromatograph. Calibration of the system is accomplished using argon standards with known concentrations of hydrogen.

2.2. MATERIALS AND RESULTS

In this section the problem of the retention of hydrogen within the

*

R and P are related simply by the conversion from mm to cm;
 $R = 10P$.

Fig. 1--Apparatus for measurement of permeability of tungsten, using tube technique

cladding of SNAP-type fuel elements by the use of metallic claddings is considered. As discussed in the treatment of permeation theory in Section 2.1, a low permeation rate of hydrogen through a metal results from either a low diffusion constant for hydrogen in the metal or a low solubility of hydrogen in the metal or both. Thus, candidate materials should be non-hydride formers with low hydrogen solubilities and materials with high melting points in which one may expect low diffusion coefficients. ⁽⁶⁾

Most of the metals in the periodic table may rapidly be eliminated from consideration as cladding materials on the basis of low melting point, high cross section, inadequate supply, high cost, or high solubility of hydrogen in the metal. Only five pure metals remain as candidates: Be, Cr, Mo, W, Si. It should be noted that the compatibility of these materials has not yet been considered. The difficulties of fabrication of these materials is also acknowledged.

If considerations of structural strength and compatibility with NaK are ignored for the moment, and attention is focused solely on the problem of hydrogen retention, the use of only three of the pure metals listed above can be seriously considered. In recent studies at Atomics International, ⁽¹⁾ molybdenum has been found to have too high a permeation rate for hydrogen for use as a pure metal cladding. No permeation data on hydrogen in beryllium seem to be available, but metallographic studies of proton-bombarded beryllium suggest hydrogen diffusion coefficients of the order of $10^{-10} \text{ cm}^2/\text{sec.}$ ⁽⁷⁾ The more serious problem for beryllium in a reactor environment is the possible formation of large amounts of helium gas due to the reactions

Estimates of the helium buildup in beryllium are in the range of 0.5 cm^3 of He per cm^3 of metal per year. ⁽⁸⁾ These are rough estimates and highly

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dependent on the neutron spectrum. At this stage, therefore, beryllium must be considered only an outside possibility. However, detailed calculations on the flux above 1 Mev will be necessary before beryllium can be completely eliminated from consideration. For the present we are thus limited to the metals Cr, W, Si. No data are available on the diffusion of hydrogen through chromium, although there is no reason to expect it to be lower than through molybdenum. In addition, the fabrication of chromium is less advanced than even that of tungsten.

Tungsten has a high melting point (which might indicate a low diffusion coefficient). It also has an unknown but reportedly low solubility of hydrogen.⁽⁹⁾ The recent possibility of obtaining seamless tungsten tubes of >99% theoretical density therefore made tungsten appear an interesting possibility for a cladding material. Accordingly, General Atomic initiated a series of screening experiments designed to determine whether or not tungsten would prove sufficiently retentive for hydrogen to permit its use as a cladding for SNAP-type fuels. The screening experiments have been carried out by totally encapsulating pellets of zirconium hydride (of the approximate composition $ZrH_{1.63}$) with about 20 mils of tungsten by a vapor deposition process. The capsules were then placed in a quartz tube and annealed at various temperatures while the hydrogen release rate was measured. The amount of hydrogen was determined by sweeping the capsule with a stream of argon and passing the effluent gases into a gas chromatograph. Release rates several orders of magnitude lower than those of the present SNAP-8 fuel specifications can be determined by this method.

While the method outlined above requires simple equipment, it suffers from the drawback that the permeation rates measured at different specimen temperatures are not at constant pressure since the equilibrium pressure of hydrogen over zirconium hydride also varies with temperature. It is possible to normalize the data to a constant pressure of 1 atm by dividing the measured release rate by the square root of the equilibrium

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hydrogen pressure. It is also possible to normalize the data to the standard cladding thickness so that the data may be compared with the SNAP-8 fuel specifications.

The data obtained to date are given in Table II and the normalized release rates are plotted in Figure 2 for comparison with the specified maximum release rates for the SNAP-8 fuel. Thus, it can be seen that General Atomic's preliminary measurements indicate that a 10-mil tungsten cladding provides an adequate hydrogen barrier for the present SNAP-8 fuel. Experiments aimed at improving both the precision and the accuracy of our data are continuing.

As the result of a failure of the temperature control equipment, some additional information on the mechanical strength of tungsten was obtained inadvertently during the course of these experiments. Both samples tested to date underwent temperature excursions of 250° - 350° C above the 800° experimental temperature; the temperature of the samples reached 1060° and 1160° C. At these temperatures, the equilibrium hydrogen pressures over $\text{ZrH}_{1.63}$ are 40 and 170 atm, respectively. The length of time at temperature is not known. The 20-mil cladding on the 1060° sample ruptured, but the appearance of the ends of the specimen (Fig. 3) makes it clear that the cladding bulged considerably before it ruptured. The second sample remained intact although the ends of the cladding underwent considerable plastic deformation. The hydrogen release rate returned to its equilibrium value as temperature and pressure equilibrium was re-established. Although quantitative data on the strength are lacking, it is clear that the vapor-deposited tungsten can withstand the hydrogen pressures generated in moderate temperature excursions without rupture, and that tungsten has sufficient ductility at temperatures of the order of 1000° C to undergo appreciable plastic deformation rather than rupture under stress. Tungsten also appears, on cursory examination of the literature, ⁽¹¹⁾ to be compatible with NaK at temperatures of interest.

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Table II
AVERAGE HYDROGEN RELEASE RATES OF TUNGSTEN-COATED ZIRCONIUM HYDRIDE

Sample No.	Temp. (°C)	Cladding Thickness (mm)	Equilibrium Hydrogen Pressure ^a (atm)	Specific Permeation Rate (cm ³ (STP)/cm ² -sec)	Normalized Permeation Rate (cm ³ (STP)-mm/cm ² -sec-atm ^{1/2}) ^b
4	848	0.508	3.80	1.43×10 ⁻⁶	3.74×10 ⁻⁷
4	801	0.508	1.74	6.81×10 ⁻⁷	2.62×10 ⁻⁷
4	775	0.508	1.10	4.54×10 ⁻⁷	4.54×10 ⁻⁷
4	745	0.508	0.62	1.64×10 ⁻⁷	1.05×10 ⁻⁷
2	846	0.508	3.54	2.25×10 ⁻⁶	6.60 10 ⁻⁷
2	795	0.508	1.55	4.54×10 ⁻⁷	2.27 10 ⁻⁷

^aCalculated from equations given in Reference 10.

^bNote that normalized membrane thicknesses in this table and Figure 2 are given in mm, in contrast to the discussion, where cm is used.

Fig. 2--Temperature dependence of permeability of tungsten to hydrogen

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Fig. 3--Tungsten-coated zirconium hydride
with "bulged" cladding

The permeation and diffusion of hydrogen through single-crystal silicon has been studied in detail by Van Wieringen and Warmoltz. (12) At 800°C the permeability of silicon to hydrogen is $8.4 \times 10^{-12} \text{ cm}^3(\text{STP}) \text{ cm} / \text{cm}^2 \text{-sec.}$ The low permeability is due primarily to the low solubility of hydrogen in silicon, $1.56 \times 10^{-7} \text{ cm}^3$ of H_2 per cm^3 of metal at 800°C. The corresponding diffusion coefficient is quite large, $5.4 \times 10^{-5} \text{ cm}^2 / \text{sec.}$ It is clear, however, that elemental silicon would form a more adequate (by several orders of magnitude) barrier to hydrogen than would even tungsten. Unfortunately, silicon is an extremely brittle material and could not presently be fabricated into a fuel element can; in all probability it would also not withstand the launch vibration; the 800°C operating temperature is high compared to the melting point of silicon; and it is questionable whether pure silicon alone would have the required high temperature structural strength. However, a sandwich-type cladding, in which perhaps 5 mils of silicon is deposited between two 5-mil tungsten layers, offers

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the excellent possibility of being an extremely retentive cladding. In addition, the tungsten overcoat appears to be compatible with NaK at temperatures up to 900°C.⁽¹¹⁾ General Atomic has an experiment under way to check the feasibility of producing the three-layer cladding and to test its permeability. Since molybdenum also offers good corrosion resistance to NaK, if silicon is used as the hydrogen barrier, a Mo-Si-Mo sandwich-type cladding may also make a promising retentive coating. In the latter case, the nuclear poisoning effect of the molybdenum would be considerably less than that of the tungsten.

The types of materials which may make suitable claddings for the zirconium hydride-base fuels have been discussed in this section; the following section, 2.3, describes a proposed set of experiments designed to evaluate the hydrogen permeability of these materials.

2.3. PROPOSED EXPERIMENTS

The experimental program which is proposed in this section is designed to evaluate the suitability of tungsten, molybdenum, silicon and beryllium and combinations thereof as cladding materials for SNAP-type fuel elements. Tungsten is considered to be the prime material on which attention should be centered because

1. Tungsten, by itself, appears to be sufficiently impermeable to hydrogen to meet current SNAP-8 fuel specifications.
2. From the cladding viewpoint, the application of tungsten involves the least new development work. Tungsten coatings are being applied almost routinely to a variety of substrates.
3. Tungsten is compatible with NaK even at 900°C.⁽¹¹⁾

Accordingly, an intensive detailed study of the diffusion, permeation, and solubility of hydrogen in tungsten is proposed. In this series of experiments the permeability of tungsten to hydrogen will be measured, using the tube technique, as independent functions of thickness, temperature and pressure. It is planned to determine whether the permeation of tungsten by hydrogen is inversely proportional to the thickness and directly proportional to both

the temperature and pressure, as required by Equation 8 in Section 2. 1. In addition, it is planned to measure the solubility of hydrogen in tungsten as a function of temperature and pressure, and to measure the permeation of hydrogen through single-crystal tungsten to eliminate the uncertainty of grain boundary diffusion. These data, along with that obtained from the permeation studies, would enable calculation of the lattice diffusion coefficient of hydrogen in tungsten.

It is important to separate and identify the diffusion and permeation processes so that the rate-limiting step of the latter is known when considering the most effective methods of decreasing the rate at which hydrogen passes through the metal. The precise measurement of these basic steps in the permeation process is more difficult than the mere determination of the rate at which hydrogen is released from a fuel element. Accordingly, once the data described above are obtained and the permeation process is understood, the less complex (and relatively inexpensive) capsule experiments can be utilized to study other variables.

In the capsule-type experiments (currently being used to screen cladding materials) a pellet of zirconium hydride is totally encapsulated with the cladding material by the vapor deposition process. The total encapsulation and the support of the pellet during the encapsulation process are facilitated by the design shown in Figure 4. While the temperature and hydrogen pressure may not be varied independently using this technique, the data can be normalized to a pressure of one atmosphere using the equations given in Section 2. 1.

The capsule-type experiments also will be utilized to study the effects of different cladding conditions on the permeation rate. The variables in the cladding process which would be investigated are the temperature of the deposition and the partial pressures of metal halide and hydrogen during the coating process. The permeability of machined, vapor-deposited surfaces would also be investigated. The synergistic effects, if any, of oxide or nitride films on the fuel rod might also be investigated in this series

Fig. 4--Schematic of specimen of $\text{ZrH}_{1.7}$ encapsulated with tungsten

of experiments. Finally, the layer-type claddings discussed in Section 2.2 can be conveniently studied using the capsule technique since a study of the effect of variations in the thickness of the layers would be desirable. The multilayer claddings presently being considered for study are:

W-Si-W	W-Be [*] -W
Mo-Si-Mo	Mo-Be [*] -Mo

A number of capsules can be investigated concurrently using the gas chromatograph since the effluent from the specimen furnaces can be sampled 24 hours a day on a programmed basis using solenoid-operated bypass and injection valves.

^{*}It is not possible, at present, to vapor-deposit beryllium. Thus, these capsules would have to be produced by vapor-plating beryllium tubing.

III. CLADDING COMPATIBILITY STUDIES

As pointed out in the discussion in Section II of the materials which might serve as a cladding for SNAP-type fuel, it is planned that either tungsten or molybdenum would be the metal exposed to the NaK primary coolant and also to the zirconium hydride fuel rod. Some work would therefore be necessary to ensure that claddings which could retain hydrogen would also be suitable for use in NaK-78 at 800°C for 10,000 hours. In addition, the cladding material must be compatible with the zirconium-uranium hydride fuel rod. This section deals with the screening studies deemed necessary to ensure that these materials are sufficiently compatible to justify further studies of metal-clad SNAP-type fuel elements.

The compatibility of the fuel rods with tungsten and molybdenum will be investigated by metallographic studies of hydride-tungsten and hydride-molybdenum diffusion couples annealed at 800°C for 1000 and 5000 hours. No difficulties or problems are expected from hydride-refractory metal interactions, but the relative ease and low cost of these experiments makes them a worthwhile part of the proposed program.

The more critical compatibility problem involves the corrosion resistance of W and Mo to NaK. The Reactor Handbook⁽¹¹⁾ reports that Mo and W have satisfactory resistance to NaK to "at least 900°C." No details of time or depth of penetration are given and, further, these data do not apply to vapor-deposited material which may have very different properties from powder metallurgy tungsten. Accordingly, a modest program of corrosion tests is proposed to check the corrosion resistance of the vapor-deposited materials to flowing NaK.

General Atomic is currently operating a NaK loop with four test legs at its Harbor Drive facility in San Diego. The loop is normally operated under isothermal conditions at 950°F, but installation of supplemental

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heaters on two of the legs will permit testing of corrosion samples at 1200° and 1400°F. Cold sections following each of the hot sections will indicate whether mass transfer is a problem. By operating the loop for 100 hours and removing half of the samples at 50 hours, it will be possible to obtain information on both the time and temperature dependence of the depth of penetration of the metals by the NaK and the mass transport, if any, of the metals from the hot to the cold zone. It is also planned to expose machined surfaces of vapor-deposited materials for 50 hours at 1400°F and 100 hours at 1200°F. Thus, differences in corrosion resistance between machined and vapor-deposited surfaces can be established by these experiments.

If the materials behave satisfactorily in these tests, a more comprehensive corrosion testing program will be necessary to proof-test the cladding for SNAP-type fuel elements.

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IV. CLADDING DEVELOPMENT

The preceding sections of this proposal have emphasized that the refractory metal claddings being considered are applied to the fuel rod by a vapor-deposition process rather than by the more usual techniques. While the art of fabrication of tungsten and molybdenum has advanced rapidly during the past five years under the impetus of the space programs, the ability to produce vacuum-tight, non-brittle, mechanically strong welds in these metals by the usual methods has still not been attained.

Seamless molybdenum tubing produced commercially for a number of years by a hot drawing process is stated to be 100% of theoretical density.

Tungsten tubing has appeared on the market only very recently, and in most cases the quality is poor; however, some manufacturers have very recently begun producing seamless tungsten tubing of high quality by a vapor-deposition process. Welds between pieces of pure tungsten can be made by vapor depositing tungsten over the weld area. The vapor-deposited weld is as strong, ductile and leak-tight as the parent metal. This does not mean, however, that vapor-deposited tungsten is a ductile metal at room temperature which can be fabricated by the usual machining techniques. Precision drilling can be done ultrasonically and with carbide tools, and the material can be ground to close tolerances. Unusual and geometrically difficult shapes can be produced directly by vapor deposition, reducing the amount of welding and machining required to produce the finished part. The vapor deposition technique, however, is not yet a production line process that can make parts with reproducible physical properties on a semi-continuous basis. It is also not clear that all vapor-deposited tungsten coatings will have the low hydrogen permeabilities reported in this document. Some development of the cladding process will therefore be necessary before cores for SNAP reactors can be fabricated utilizing this technique. This section of the proposal discusses the cladding development program

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necessary to ensure that reproducible, hydrogen-impermeable claddings can be deposited on a routine basis.

A basic objective of the cladding development program is to determine the optimum conditions for the deposition of claddings as functions of the temperature of deposition, the rate of deposition, and the partial pressures of the hydrogen and refractory halides. The relationship between these variables and the crystallite size is also important. This part of the program therefore proposes the production of claddings, deposited under controlled conditions of temperature, pressure and flow rate, whose properties will be studied under other parts of this program. The crystallite size will be determined metallographically and the permeability will be determined using the capsule technique. As a minor part of this program, the mechanical properties of the cladding--such as ultimate tensile strength, yield strength, and creep properties--should also be measured. The machining properties of the materials should also be investigated. The mechanical and machining properties studies would be a very small and cursory portion of the program, the major effort being devoted to the study of the cladding process.

The tungsten cladding is normally applied by the reduction of WF_6 by hydrogen on the substrate which is held at 600° - 800° C. Molybdenum is deposited from the pentafluoride in the same manner, but at substrate temperatures of 750° - 900° C. A schematic diagram of a typical vapor-plating apparatus is given in Figure 5. Frequently, the quality of the deposits from the vapor plating operation are non-uniform, and the effects of the process variables are not well understood. The material produced by one organization may be far superior to that produced by another also technically competent group.

General Atomic proposes to investigate the following variables in the coating process:

1. The temperature of the substrate during deposition
2. The partial pressure of the metal halide

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Fig. 5--Schematic of typical vapor-plating apparatus

3. The partial pressure of hydrogen
4. The flow rate of the gases
5. The use of metal halides other than the fluoride.

The effect of several of these factors has been discussed for the case of the iodides by Rolsten.⁽¹³⁾ Thermodynamic considerations govern the minimum temperature at which the metal will deposit. At temperatures below this minimum, reactions of the type

may take place, with consequent attack of the deposit or even the substrate. At temperatures above the optimum, coarse crystalline growth occurs, rather than smooth layer deposition.

Many metals can be vapor deposited without the use of hydrogen by a simple thermal decomposition process. Hydrogen, however, does lower the minimum deposition temperature, and, indeed, in the case of coating hydrides substrates which have fairly substantial equilibrium pressures of hydrogen at moderate temperatures, the hydrogen partial pressure is essential to prevent dissociation of the hydride.

The partial pressure of the metal halide (and also the flow rates) governs the rate at which metal is deposited. Very slow growth and the deposition of very large crystals is not desired but, conversely, neither is very rapid deposition of a "snow" with low density.

Since metal halides other than the fluoride would be expected to decompose at lower temperatures, some advantage might be gained in coating hydride fuels by the use of one of the other halides, provided an acceptable deposit can be produced.

V. ANCILLARY STUDIES

On the basis of some rather simple arguments it appears that tungsten cladding can be used on the U-ZrH fuel elements, even for intermediate energy spectrum reactors, without an unacceptable increase in the fuel inventory. Some estimate of the penalty can be made from the methods and data contained in Chapter 7 of the Naval Reactors Physics Handbook, Vol. 3. (14)

Equation 7.24 in that reference indicates a method for estimating the incremental fuel load required to compensate the addition of a poison. Converting the equation to give masses in grams instead of moles, the expression becomes

$$\Delta M_f = \frac{A_f}{A_a} \frac{\sigma_a}{\sigma_f} \frac{\overline{F}_{L_a}}{1 - (1 + \alpha) \overline{F}_{L_a}} \Delta M_a$$

where

A_f	=	atomic mass of fuel,
A_a	=	atomic mass of absorber,
$\overline{F}_{L_a} \approx \overline{F}_L$	=	iterated fission probability of the absorption energy neutrons for either the poison or the fuel, and
σ_a / σ_f	=	the ratio of the spectrum-averaged cross sections for absorption in the poison and fission in the fuel.

For the type of reactor under consideration, typical values for these parameters are as follows:

A_f / A_a	=	$\frac{235}{184} = 1.28$
σ_a / σ_f	=	0.4 (see data in Table 7.2 of reference)
$\overline{F}_L$	=	0.6
$1 + \alpha$	=	1.3.

Using this data we find that

$$\Delta M_f = 1.4 \Delta M_a$$

which is probably accurate to $\pm 30\%$.

Using this procedure it is found that a 0.010" tungsten cladding on the 211 fuel elements would require 0.65 kg of tungsten, and therefore, about 0.9 KG of fuel over the basic inventory. Likewise, a 0.020" tungsten cladding would require an extra 1.8 kg of fuel.

It is emphasized that the above results are based on some very crude methods for estimating the fuel requirements. As part of the proposed program a more accurate evaluation of the fuel penalty would be undertaken. Multigroup calculations of the dependence of fuel inventory on the tungsten loading will be carried out.

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VI. STATEMENT OF WORK

The following statement of work is proposed for incorporation in any contract resulting from this proposal:

"The contractor will expend its best efforts in a program of research and development on hydrogen retentive claddings for uranium-zirconium hydride fuel elements, utilizing pure metals and combinations of metals with other metals, or metallic-life elements.

The program will include but will not necessarily be limited to:

- A. Hydrogen Retention Studies
 - 1. Study the rate of permeation of hydrogen through metals and combinations of metals which show promise of being effective barriers for hydrogen.
 - 2. Investigate the effects of multilayer metallic structures, crystallite size, and conditions of deposition of metallic claddings on the rate of hydrogen permeation through the claddings.
- B. Cladding Compatibility Studies
 - 1. Conduct preliminary screening experiments on the compatibility of the cladding materials with both zirconium hydride and NaK.
- C. Cladding Development Studies
 - 1. Carry out developmental studies on the effect of process variables on the quality of metallic claddings deposited on a hydride substrate by the vapor deposition technique.
- D. Nuclear Physics Analysis
 - 1. Perform preliminary calculations on the effects of cladding materials on the reactor physics and heat transfer properties of the reactor system. "

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VII. PERSONNEL

This section contains resumes and qualifications of the personnel who are expected to be active in the conduct or supervision of the program:

Dr. Edward L. Brady

B. A. (Chemistry), U. C. L. A. , 1940

M. A. (Chemistry), U. C. L. A. , 1942

Ph. D. (Physical Chemistry), M. I. T. , 1948

From 1942 to 1946, Dr. Brady was a member of the Fission Products Group of the Manhattan Project, working both at the Metallurgical Laboratory of the University of Chicago and in Oak Ridge. From 1948 to 1959, he was associated with physical chemistry programs in the General Electric Research Laboratory and at the Knolls Atomic Power Laboratory in Schenectady, New York. Prior to joining General Atomic, Dr. Brady served for two years as Senior Scientific Advisor on the U. S. Mission to the International Atomic Energy Agency, stationed in Vienna, Austria.

At General Atomic, Dr. Brady is Assistant Chairman of the Chemistry Department and Group Leader of the Materials Chemistry Group.

Mr. Robert J. Campana

B. S. (Engineering Physics), University of Maine, 1949

Diploma in Nuclear Engineering, Oak Ridge School of Reactor Technology, 1953

In 1949, Mr. Campana joined the staff of the Atomic Power Department of the Allis Chalmers Manufacturing Company, where he participated in experimental research and development of mechanical and electro-magnetic pumps for reactor cooling applications and studied cavitation corrosion in liquid metals. In 1951 he joined the staff of Mine Safety Appliance Company, where he performed and supervised experimental research relative to liquid-metal, pressurized-water, and organic-moderated reactors. While with

Mine Safety Appliance Company he was co-author of the instrumentation section of the USN-AEC Liquid Metals Handbook.

From 1956 to 1959, Mr. Campana was with Douglas Aircraft Company, where he participated in aircraft nuclear propulsion application studies on a wide variety of missile, vehicle, and power-plant types. He also assisted in forming an ANP Nuclear Analysis group and acted as general nuclear consultant to the engineering and safety departments.

At General Atomic, Mr. Campana is a member of the Direct Conversion Project. He has worked on the design of solar thermoelectric power devices and on liquid-metal pumps for thermionic reactors. He is presently principal investigator of a project to develop a liquid-metal heated thermoelectric space power generator for the U. S. Navy Bureau of Weapons. As Head of the Thermoelectric Devices group, he has supervised the design of a variety of thermoelectric devices.

Mr. Stanley E. Donelson

M. E. (Metallurgy), Rensselaer Polytechnic Institute, 1947

Mr. Donelson was employed at the National Lead Company plants in Ohio and New Jersey from 1949 to 1956 as plant engineer and superintendent of the lined product department, respectively. For the next two years, at NRC Equipment Corporation, he was a project engineer engaged in development and production of high-vacuum equipment. From 1958 until he joined General Atomic in 1962, to assume duties as Manager, Fabrication, he was head of the reactor fuel materials group of the M and C Nuclear Engineering Section.

Dr. Sidney Langer

A. B. (Chemistry), New York University, 1949

Ph. D. (Chemistry), Illinois Institute of Technology, 1955

Before joining General Atomic, Dr. Langer was a physical chemist at Oak Ridge National Laboratory, where he worked on the molten-salt reactor project from 1954 to 1960. Dr. Langer's work consisted of vapor-pressure, surface-tension, and cryoscopic measurements of molten-salt systems, and the determination of activities in solid-metal alloys by electromotive-force methods.

At General Atomic, Dr. Langer is doing high-temperature chemistry work on the high-temperature graphite-moderated power reactor program. Specifically, he has been engaged in the experimental study of phase relations in systems containing uranium-thorium-carbon and fission products. He has also been interested in the thermodynamic properties of carbides and their vaporization processes. Dr. Langer has carried out the preliminary experiments on hydrogen retentive coatings described in this proposal.

Dr. U. Merten

B. S. , California Institute of Technology, 1951

Ph. D. (Radiochemistry), Washington University, 1955

Dr. Merten came to General Atomic from the Knolls Atomic Power Laboratory, where he worked on physical chemistry problems of the Submarine Intermediate Reactor and the Submarine Advanced Reactor projects.

At General Atomic since 1956, Dr. Merten participated in reactor development programs and has carried on experimental investigations of chemical equilibria at high temperature and the chemistry of certain semi-conducting compounds. He currently heads General Atomic's study of water desalination using reverse osmosis and is Assistant Chairman of the Chemistry Department. He is the co-author of several publications on zirconium hydride fuels research and production.

Dr. David V. Ragone

Ph. D. (Metallurgy), Massachusetts Institute of Technology, 1953

Dr. Ragone served as assistant professor of metallurgy at the University of Michigan from 1953 to 1957, as an associate professor from 1957 to 1961, and became a full professor in 1961. In 1960 he spent a sabbatical leave at the Imperial College of the University of London.

Dr. Ragone has been a consultant to General Atomic since 1958, and joined the staff full time in 1962 as Chairman of the Metallurgy Department. In this position, he is in charge of General Atomic metallurgy research and development programs, with emphasis on high-temperature materials development for advanced power generation and energy conversion systems. He is also responsible for the fabrication of fuel materials and fuel elements, including U-Zr-H elements used in General Atomic TRIGA reactors.

Dr. Hugh B. Stewart

B. S. (Physics), Kent State University, 1938
M. S. (Physics), Ohio State University, 1939
Ph. D. (Physics), Ohio State University, 1947

From 1941 to 1946, Dr. Stewart was on the staff of the Allison Division of General Motors Corporation. In 1947 he joined Knolls Atomic Power Laboratory as a research associate working on critical experiments. Subsequently he served as supervising physicist of critical experiments in the Experimental Physics Unit and later as manager of critical experiments. He also held positions as Manager, SIR Project Physics; Manager, Advanced Development Physics; and Manager of DIG Project Physics.

At General Atomic Dr. Stewart has been physics task leader for the Peach Bottom Project as well as Chairman of the Department of Nuclear Analysis and Reactor Physics.

Dr. A. F. Weinberg

B. S. (Metallurgy Engineering), Illinois Institute of Technology, 1952
M. S. (Metallurgy Engineering), Illinois Institute of Technology, 1953
Ph. D. (Metallurgy Engineering), Illinois Institute of Technology, 1960

While working toward his Master's degree, Dr. Weinberg taught metallurgical engineering courses at the Illinois Institute of Technology, and while working toward his doctorate he held a research fellowship, under which he did research in developing the Mg-Li-Zn phase diagram. From 1957 to 1959, at Armour Research Foundation as a research metallurgist, he worked on fuel solutions for the liquid-metal-fuel reactor experiment, solid-solution strengthening of Mg alloys, brittle fracture, and the effect of neutron irradiation on niobium. In the Advanced Research group at Solar Aircraft Company in 1959 and 1960, Dr. Weinberg worked on problems of fracture, improving the strength of high-strength steels, and preliminary design of advanced space systems.

At General Atomic since 1960, Dr. Weinberg has been engaged in studies of the high-temperature properties of metals and graphites, gas-metal interactions, fundamental problems in mechanical metallurgy, including radiation effects, and fabrication of refractory metal and refractory metal carbide materials.

Mr. Paul D. Wright

B. S. (Chemical Engineering), University of Michigan, 1951
B. S. (Metallurgical Engineering), University of Michigan, 1951

Mr. Wright was an engineer with the General Electric Company at Richland, Washington, from 1951 to 1956, when he transferred to General Electric's Metallurgical Products Department in Detroit, Michigan. In 1957, he went to General Electric's San Jose plant as a powder metallurgy process manufacturing engineer.

At General Atomic, Mr. Wright is doing research in the Metallurgy Department, primarily on metallurgy and materials problems. He is also responsible as Supervisor, Special Projects, for the fabrication of U-Zr-H fuel elements used in the General Atomic TRIGA reactors.

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VIII. CONTRACTUAL INFORMATION AND COST ESTIMATE

This proposal is submitted on contemplation of support under a cost-plus-fixed-fee contractual arrangement. For the initial 12-month program described in this proposal, the estimated cost including fee is \$164,375. A cost estimate for this 12-month effort is tabulated on the next page.

General Atomic certifies that the labor rates used in the cost estimate are current and in accordance with rates approved by Government agencies. General Atomic's wage and salary rates are submitted periodically for review and approval to the Atomic Energy Commission and to the San Diego Air Force Contract Management District.

The overhead rates used in the cost estimate consist of all General Atomic Division indirect expenses, adjusted for assumed unallowable costs and projected over the proposed contract period. Indirect expenses at General Atomic are collected into burden pools, distributed on the basis of burden-center direct labor dollars. This method for the distribution of indirect expenses has been submitted for review and approval to our cognizant audit agency, the San Francisco Operations Office of the Atomic Energy Commission.

The hourly rental rate for the IBM 7090 computer at General Atomic is an estimated provisional direct cost. This rate will be adjusted at the end of each calendar year to actual cost based on Government audit. The rate does not include a profit factor.

The entry in the cost estimate for special-purpose equipment includes the estimated cost of the necessary furnaces, controller, recorder, gas chromatograph and peripheral equipment, vacuum equipment, heat exchangers, and heaters.

Unless previously withdrawn in writing, this proposal will remain valid for 120 days from the date on the cover. However, should additional time be required in the evaluation of the proposed program, General Atomic will be pleased to consider an extension of the validity period.

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COST ESTIMATE FOR TWELVE-MONTH PROGRAM

Personnel Services		\$50,360
Research and Development Staff Members, Chemistry	11 man-months	
Research and Development Staff Associates, Nuclear Analysis and Reactor Physics	2 man-months	
Research Assistants, Chemistry	24 man-months	
Technicians, General Engineering	3 man-months	
Technicians, Chemistry	15 man-months	
Technicians, Metallurgy	5 man-months	
Technical Editing	2 man-months	
Machinists, Shop	3 man-months	
Overhead		71,150
General Laboratory, at 140%		
Shop, at 175%		
Payroll Expense, at 5.7%		2,871
IBM 7090 Computer Rental, 3.5 Hours at \$608/hr		1,824
Materials and Supplies		9,000
Special Purpose Equipment		10,900
Subcontract		3,000
Travel		920
Communications		125
Consultants' Fees and Expenses		<u>1,000</u>
TOTAL ESTIMATED COST		\$151,150
FIXED FEE		<u>13,225</u>
TOTAL ESTIMATED COST PLUS FEE		\$164,375

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