ENTRAPMENT OF KRYPTON IN SPUTTER DEPOSITED
METALS--A STORAGE MEDIUM FOR RADIOACTIVE GASES

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SUMMARY

Sputter deposition of metals with a negative substrate bias results in a deposit containing relatively large concentrations of the sputtering gas. This phenomenon has been applied as a technique for storage of the radioactive gas, ^{85}Kr , which is generated in nuclear fuels for power production. Alloys which sputter to yield an amorphous product have been shown to contain up to 12 atom% Kr [42 cm³ of Kr(STP)/g of deposit; concentration equivalent to a gas at 4380 psi pressure]. Release from these metals occurs at so low a rate that extrapolation to long times yields a ^{85}Kr release at 300°C of about 0.06% in 100 years.

A preliminary evaluation of the engineering feasibility and economics of the sputtering process indicates that ^{85}Kr can be effectively trapped in a solid matrix with currently available techniques on a scale required for handling DOE generated waste or commercial reprocesses fuels and that the cost should not be a limiting factor.

TABLE OF CONTENTS

SUMMARY.	ii
INTRODUCTION	1
GAS ENTRAPMENT DURING SPUTTERING	2
EXPERIMENTAL PROCEDURES - - - - -	6
SPUTTER DEPOSITION.	6
KRYPTON RELEASE MEASUREMENTS	9
RESULTS AND DISCUSSION - - - - -	10
SPUTTER DEPOSITION OF CRYSTALLINE DEPOSITS	10
SPUTTER DEPOSITION OF AMORPHOUS DEPOSITS	11
GAS RELEASE MEASUREMENTS.	11
ENGINEERING FEASIBILITY AND ECONOMIC ANALYSIS.	20
CONCLUSIONS. . .	25
ACKNOWLEDGMENTS.	
REFERENCES .	27
APPENDIX	A-1

INTRODUCTION

Several inert gas isotopes are generated by the fission of uranium in nuclear reactor fuels. Of these isotopes, many are non-radioactive or have very short half-lives and decay soon after the fuel is removed from the reactor. Krypton-85, thus, remains the only inert gas isotope of concern for long-term storage of nuclear wastes. Krypton-85 emits a beta particle with a maximum energy of 0.66 MeV and a very low flux of 0.52 MeV gamma rays. It has a half life of 10.76 years.

The chemical inertness of krypton reduces markedly the biological effects of ^{85}Kr and, therefore, release of small quantities to the atmosphere has been permitted. Federal regulations, (1) to take effect in 1983, limit the release of ^{85}Kr to $50,000 \text{ Ci}/10^9 \text{ Watt years}$ of electrical energy or about 15% of the total ^{85}Kr produced in light water reactor (LWR) fuels. To **meet this requirement, studies are underway to develop the most appropriate** means to collect, separate, and store the ^{85}Kr generated in nuclear power plants. Several methods have been proposed for storage of ^{85}Kr including gas bottle storage, immobilization in the pores of molecular sieves, dissolution in glass or other solids, ion implantation into metals, storage in gas pockets underground, and others. An evaluation of those processes presently receiving the most attention was recently completed by Knecht. (2)

One of these techniques, ion implantation in metals, is currently under investigation in our laboratory and is the subject of this report. The purpose of this document is to describe the rationale for this approach and the results of our investigation to date. Also included in this report is a preliminary evaluation of the economics of this process for comparison with other potential ^{85}Kr storage methods.

GAS ENTRAPMENT DURING SPUTTERING

Gases can be implanted into solids by bombarding their surfaces with energetic ions. (3-6) For Kr^+ the depth of implantation is energy dependent and amounts to only a few atom layers at energies in the keV range. Thus, to produce bulk amounts of a solid containing high concentrations of Kr, it is necessary to perform the implantation during film growth by a vapor deposition process such as sputtering. Many examples of gas incorporation by these techniques have appeared in the literature during the past few years. (7-9) Sputtering of solids appears to be particularly well suited for gas incorporation where the sputtering ion is generated from the gas which is to be implanted into the solid.

Early researchers have shown that sputtering is a momentum transfer process (10,11) as illustrated in Figure 1. Positively charged ions are accelerated to the surface of the target and sufficient energy is transferred to overcome the binding energy of the atoms in their lattice. Sputtering yields, defined as the ratio of the number of ejected atoms to that of incident ions, are dependent upon the binding energy of the target atoms and the mass and energy of the bombarding ions. These yields may vary over a wide range from much less than one to as high as 15 for silver bombarded with 10 keV Kr^+ . (12)

In order to achieve a practical deposition rate, a dense plasma adjacent to the target is required. In our system, this is achieved by producing a thermionically supported plasma in the annulus between the target and a substrate as shown in Figure 2. The positive ions are formed by collisions between energetic electrons and krypton gas atoms, and are accelerated to the target surface by applying a large negative voltage to it. The sputtered atoms leave the target with approximately a cosine spatial distribution and deposit uniformly on the substrate when the proper geometrical relationship between the target, substrate, and shields has been achieved.

In most applications of sputter deposited metals, attempts are made to minimize the gas incorporated in the deposit to obtain the desirable properties. However, in our process, where the purpose of sputtering is to

FIGURE 2. Thermionically Supported Plasma Sputtering/Ion Implantation Components

trap gas in the deposited material, we must adjust the parameters to obtain maximum gas content. It has been shown(8) that the gas content is increased markedly by applying a negative bias to the substrate, thus accelerating Kr⁺ to the substrate as well as to the target. Of course, the substrate voltage, relative to the target voltage, must be maintained at a ratio which will yield a net deposit on the substrate. Other sputtering parameters such as deposit composition and microstructure, electrode voltages and current densities, substrate temperature, and system geometry also affect the gas trapping rate and are adjusted to yield the desired result. Recently, Cuomo and Gambino(13) have reviewed the status of inert gas sputtering and correlated the gas trapping coefficient with a number of the sputtering parameters. In particular, Cuomo and Gambino showed a large increase in gas trapping when sputtering amorphous films. They reported achieving gas loadings as high as 13 atom% for Ar and Kr and up to 28 atom% for Ne in an amorphous alloy of nominal composition Gd_{16.5}C₀₆8.5Mo₁₅'

These data and others in the literature clearly show the potential for trapping inert gases and it was recognized that this approach may yield an excellent means of long-term storage of gaseous nuclear fission products. This approach has distinct advantages in that there are no high temperature structural materials problems and all operations are conducted at low pressure (~1 Pal when compared to other possible alternatives which require systems capable of operation at temperatures of 500°C or above and pressure up to 20 MPa. This program was, therefore, undertaken with the major objectives as follows:

- 1) Adapt the current sputtering technology to a high rate sputtering/ion implantation process.
- 2) Find a suitable solid matrix for trapping the gas.
- 3) Determine the potential for release of the incorporated Kr as a function of temperature.
- 4) Determine the limits of scale up and perform meaningful cost/benefit studies.
- 5) Evaluate any detrimental effects from radiation or Rb buildup in the sputtered product.
- 6) Test the process using 6% ⁸⁵Kr in Kr.

This program was initiated in July 1976, and is continuing to accomplish these objectives.

EXPERIMENTAL PROCEDURES

SPUTTER DEPOSITION

The details of the sputtering process have been reported earlier. (14) However, a brief description is included here to aid the reader in understanding the process.

The sputtering apparatus designed for this project was of the thermionically supported discharge type. The general arrangement is shown in Figure 3. The cylindrical substrate, fabricated from six-inch copper pipe, was used as part of the vacuum wall to facilitate water cooling. The hardware shown in Figure 3 was mounted on our standard sputtering base assembly (14) containing the electron source, power and cooling water connections, and the pumpout port. The centrally located water-cooled target was fabricated either by drilling a hole in a cylindrical bar of the selected metal or by using a pipe of sufficient wall thickness and strength to maintain the vacuum during the entire run. Some binary metal targets were prepared by drilling holes into the wall of a cylinder of the same composition as the major component of the desired metal deposit. Small slugs (~ 0.5 cm diameter) of the minor component were pressed into the holes. The size and distribution of the metal slugs were selected to yield a homogeneous sputtered solid with the desired composition. Other binary metal targets were fabricated from commercially obtained castings of the desired alloy. Ternary targets were fabricated by adding smaller slugs (~ 0.25 cm diameter) to the targets that contained slugs or by spotwelding thin (~ 0.25 mm) wafers onto the surface of the cast targets. The target was attached to the base assembly via an electrically insulated feed-through. The gas inlet valve is a VEECO PV-10 controlled automatically to maintain a constant pressure near the electron source. In addition to the valve, the krypton passes through a Hastings-Raydist Model ALK-50 mass flow meter with a rating of 0 to 69.5 ± 0.4 cm³ of Kr at STP/minute. Typical sputtering parameters for the laboratory scale apparatus are given in Table 1.

FIGURE 3. High-Rate Sputtering/Ion Implantation Apparatus

TABLE 1. Typical Deposition Parameters

	<u>Crystalline Metals</u>	<u>Amorphous Metals</u>
Auxiliary Anode to Filament Voltage	-30 V	-30 V
Auxiliary Anode to Main Anode Voltage	+7 V	+7 V
Auxiliary Anode to Target Voltage	-2.5 V	-2.5 V
Auxiliary Anode to Substrate Voltage	-2.5 kV (pulsed)	300 V (continuous)
Filament to Main Anode Electron Current	50 amps	50 amps
Filament to Auxiliary Anode Electron Currents	5 amps	5 amps
Target Ion Current	4 amps	4 amps
Substrate Ion Current	7 amps	4 amps
Manifold Pressure	.40 Pa	.40 Pa

The dependent variables are krypton gas flow rate and material deposition rate at the substrate. The ratio of these two variables is the instantaneous concentration of krypton in the metal. To obtain the flow rate, the meter reading due to the throughput of the dynamically pumped system with no sputtering is subtracted from the reading during the runs. Multiplying this difference by the meter sensitivity factor for Kr (1.39), gives the rate of gas incorporation in the deposit directly in cm^3/min STP. The deposition rate is obtained by calculating the material arrival rate at the substrate using the sputtering yield, target/substrate geometry, and sputtering parameters of the system. The calculation provides the average deposition rate in grams/min, so that the concentration is obtained. The actual gas content, at a particular position on the substrate, is determined by gas release analysis in conjunction with x-ray fluorescence spectroscopy since some variability in gas content occurs in the sputtered deposit. The average gas content for an entire deposit is calculated by integrating the krypton flow and dividing by the substrate weight gain.

As mentioned earlier, a negative bias voltage must be applied to the substrate to obtain maximum gas trapping; yet this bias must be maintained at a low enough level to insure a net transport from the target to the

substrate. For the single component metals, a bias voltage of -2.5 kV was applied. This voltage was pulsed with the pulse duration and waveform being experimental variables. For the multicomponent metal targets yielding amorphous deposits, optimum trapping was obtained with up to -300 volts continuous bias on the substrate.

A typical run sequence is as follows: The substrate was etched with 100 eV ions at a current density of 5 mA/cm^2 for five minutes. The target voltage is raised to full value at the rate of 40 volts/min. Then the substrate bias is slowly increased until the maximum flow rate is attained. By adjusting the pulse time and period, and the substrate voltage, the gas trapping rate is maximized. During the diagnostic and sputtering parameter optimization phases of this work, information about the sticking coefficient of these metals was also obtained.

KRYPTON RELEASE MEASUREMENTS

Total Kr content is most accurately determined by measuring the quantity of gas released during high temperature treatment of the deposit. These data, from samples which have been analyzed by x-ray fluorescence spectroscopy, are required to provide the calibration for the x-ray fluorescence measurements. In addition, the rate of release of Kr as a function of temperature must be determined to evaluate the applicability of the process for storage of ^{85}Kr . A schematic of the Kr release apparatus is shown in Figure 4. Weighed samples of the sputtered metal, usually attached to the copper substrate were suspended in a mullite tube with a standard taper joint. The standard taper was mated to a water cooled pyrex joint and attached to a vacuum system capable of maintaining a vacuum of better than 10^{-4} torr. This system was heated by placing the mullite tube in a tube furnace with a temperature rating of 1300°C . The temperature was both controlled and monitored by Pt/Pt--10% Rh thermocouples attached to the outside of the mullite tube. The temperature in the inside of the tube was checked by comparing the thermocouple reading with that of a thermocouple placed in the center of the tube over the entire temperature range of interest. The samples temperature agreed with the thermocouple reading to within $\pm 10^\circ\text{C}$ over the entire temperature range when heated or cooled at typical rates.

FIGURE 4. Gas Release Analysis

As gases were released, they were pumped via a toepler pump into a calibrated volume of the vacuum system and the pressure continually monitored and recorded on either a 10 torr or 100 torr head of a ZOO series MKS capacitance manometer. Since the evolved gases are not pure Kr, they were analyzed on a Varian gas chromatograph equipped with dual columns and dual helium ionization detectors. The gases were separated on either a Z.5 m 5A molecular seive or a 1.8 m porapac N chromatographic column. The chromatographic trace of the gas, sampled at a carefully measured pressure, was compared with that of an analyzed standard to determine the partial pressure of the various components. In this system, HZ' OZ' NZ' Kr, CH₄, CO, and CO_Z are analyzed. Water vapor was eliminated by pumping the gas through a trap held at -78°C. Often small amounts of longer retention time peaks are evident but the sum of the partial pressures of the measured components usually account for better than 80% of the total gas pressure. The gas analysis of the Kr is considered to be accurate to better than $\pm 5\%$, which is more than adequate for the purpose of this study.

RESULTS AND DISCUSSION

SPUTTER DEPOSITION OF CRYSTALLINE DEPOSITS

The detailed results of this work have been published previously. (15) A brief description is given here for completeness. The initial experiment was conducted using black iron water pipe as a target while sputtering with a continuous substrate bias of up to -168 volts and 6.6 amps. Under these conditions, no detectable Kr trapping was observed on the mass flow meter. It thus became clear that the Kr⁺ sticking coefficient, w_s ' must be increased. Experiments were then performed in which the substrate bias was increased to -Z500 volts at which point substantial Kr uptake was observed. With this high substrate bias, it is necessary to pulse the substrate voltage to obtain a net deposition on the substrate. Since w_s is extremely ion energy dependent in the range from 0 to Z500 eV, the highest average w_s is obtained when the bias is applied in the square waveform with the maximum voltage being applied during essentially the entire pulse period.

The pulse duration is also of important to assure that the saturation dose (N_{TS}) is not achieved during the pulse which causes the trapping to be less efficient. Using the theory of Carter, Colligan, and Leek, (5) we estimated the time required to saturate the surface with 2 keV Kr⁺ to be 0.32 seconds. For both Fe and Ni, we estimated $N_{TS} > 10^{15}$ atom/cm² in the pulsed mode; but for maximum trapping, the ion dose per cycle should be $< 10^{16}$ ions/cm². This is achieved by decreasing the substrate pulse length as the current-density is increased. Thus, high current density need not be a limiting factor in trapping gas during the sputtering process. By manipulating the deposition parameters, deposits with relatively high Kr loadings were achieved using Fe, Al, Ni, and Ti targets. A comprehensive discussion of the sputtering conditions and parameter has been published previously, (15) but a summary of these results is presented in Table II. The highest gas content was observed in the steel deposit, followed by Ni, Al, and Ti in descending order. The Kr contents for the various metals are not optimized and thus are not directly comparable.

Our studies also yielded information on the trapping coefficient as a function of ion energy. In none of these crystalline metal deposits were we able to achieve $\omega_s > 0.1$ atoms/ion until the substrate bias exceeded -1000 volts. Thus, a major concern in developing a commercial scale sputtering system utilizing crystalline materials was the non-availability of high current equipment for rapidly pulsing the substrate voltage. Equipment with the required switching capabilities was developed up to the prototype stage on this program. Further development was postponed until amorphous metals were investigated which appeared to not require the pulsing technique.

SPUTTER DEPOSITION OF AMORPHOUS DEPOSITS

Earlier results from our laboratory (16) along with the high Kr loadings reported by Cuomo and Gambino (13) for bubble memory devices, encouraged us to investigate metals which we believed would yield an amorphous deposit. This, we assumed, would enable larger quantities of gas to be trapped with less metallic material and power consumption. In identifying potential

TABLE II. Sputtering Conditions and Kr Content in Crystalline Metals

<u>Materi al</u>	<u>Substrate Bias Current Type</u>	<u>Target Bias Current Type</u>	<u>Gas Flow cm³ min</u>	<u>Depos it i on Rate nm/see</u>	<u>Gas cm³ g</u>	<u>Content at%</u>
Nickel	1500V 7amp pulsed	2500V 4amp continuous	4.0	6.05	16.9	4.5
Alumi num	1300V 7amp pulsed	2700V 4amp continuous	2.3	5.0	30.1	3.9
Iron	2500V 2.2amp pulsed	2500V 1.25amp continuous	1.74	2.65	19.8	5.1
Titanium	2300V 5amp pulsed	2500V 4amp continuous	1.6	4.1	17	3.7

amorphous deposits, we concluded that alloying group VIII elements, i.e., Fe, Co, and Ni, with elements from group IIIB, IVB, VB or VIS had some probability to yielding a sputtered product which was non-crystalline (amorphous). Because of previous work at our laboratory,(17) we chose an Fe-Y alloy for our initial experiment. In subsequent experiments, we have studied a variety of alloys containing Fe-Si, Fe-Si-Ta, and Fe-Zr. The results from the sputter deposition of these alloys is shown in Table III. The benefits of the increased gas uptake are obvious from the table. Those alloys which have negligible Kr content were shown to be crystalline by X-ray diffraction analysis. It should be understood that the Kr content of the amorphous metals in Table III cannot be compared directly with those of the crystalline metals in Table II because the sputtering conditions were markedly different. In particular, the substrate voltage for the amorphous metals was always below -300V compared with -2500V for the crystalline metals. The lower substrate voltage is a major advantage reducing the power requirements by more than a factor of three and also eliminating the necessity for high current pulsing circuits. Also evident from Table III is the unpredictable nature of an added element to the alloy. For example, small amounts of Ta added to the Fe-Si alloy increased the Kr uptake markedly; but when a similar quantity was added to the much more effective trapping alloy of Fe-Zr, a significant decrease in Kr trapping rate was observed.

The results shown here along with those reported by Cuomo and Gambino(13) have demonstrated the ability to effectively trap inert gas ions in amorphous metal matrices. The Kr release characteristics and economic evaluation will be treated in subsequent sections of this paper.

GAS RELEASE MEASUREMENTS

The gas release measurements from sputter deposited crystalline metals (Fe, Al, Ni) were performed by heating the sample while increasing the temperature at a linear rate of about 3°C/minute. During the heating cycle, the gas was continually removed for gas analysis. At lower temperatures the gases were primarily H₂ and CO and contained practically immeasurable quantities of Kr. Significant Kr release occurred at about 600°C for Fe and

TABLE III. Experimental Summary--Amorphous Alloy Development-85 Kr Storage

Material	Gas Flow cm^3/min	Substrate Voltage (continuous)	Deposition Rate nm/sec	Average (1) Krypton Content $[\text{cm}^3/\text{g}]$ [at%]		Krypton Content(2) $[\text{cm}^3/\text{g}]$ [at%]	
FeO.85YO.13Me*0.02	12.5	-225V	8.0	31. g	9	29.5	8.2
FeO.95YO.03MeO.02	< 0.02	-250V	7.0	(3)			
FeO.69SiO.25MeO.06	< 0.02	-200Y	14.0	(4)			
FeO.67SiO.24TaO.03MeO.06	0.14	-225V	33.0	0.64		(5)	
FeO.67SiO.24CrO.04MeO.05	Experiment aborted: Deposit peeled badly						
FeO.78ZrO.20MeO.02	8.1	-240Y	15.0	18.5	5.4	15.4	4.3
FeO.26ZrO.73MeO.01	5.6	-160Y	11.0	22.1	8.1	(5)	
FeO.72ZrO.21TaO.05MeO.02	5.0	-220Y	11.0	15.7	4.9	(5)	

*Me implies minor or impurity elements

(1) Determined from total Kr uptake and total metal deposited.

(2) From small samples measured by gas release.

(3) Not calculatable due to experimental problems.

(4) Negligible

(5) Not determined.

Ni samples and at about 300°C for Al. The total Kr content was determined by integrating the Kr release over the entire temperature range and is given in Table II.

Initial gas release measurements for the amorphous deposits were also performed by programming the temperature as described above. Such measurements are useful in determining the general character of gas release from the samples, for measuring the total gas content, and for providing a calibration for x-ray fluorescence measurements, but the long-term release of radioactive gas expected during storage of the radioactive waste requires a much more careful evaluation at lower temperatures. We have, therefore, measured the release of Kr from two amorphous deposits (FeO.79YO.12KrO.09 and FeO.7SZrO.19KrO.06) by holding the samples at constant temperature in the range from 200 to 500°C for long periods of time (4 to 60 hours) and for shorter periods (0.5 to 1 hour) at temperatures above 500°C. The gas release data are shown graphically in Figures Sand 6 for FeO.79YO.12KrO.09 and FeO.7SZrO.19KrO.06' respectively. The figures are plots of the logarithm of the fractional release rate as a function of 1/TOK. This type of plot is selected to reflect the temperature coefficient of Kr release so that extrapolation to lower temperatures is possible. Within the scatter in the data, a linear plot is a reasonably good representation of the release rate at higher temperatures. At lower temperatures the release rate deviates from the linear plot, yielding rates up to three orders of magnitude faster than predicted by extrapolation of the linear plot. These relatively high rates at the lower temperatures are initial rates which decrease with time to a steady state rate before more than 0.1% of the total Kr is released. Figures Sand 6 also show data points of release rates, after from 24 to 60 hours of release at constant temperature, which approach the rate predicted by the linear extrapolation of the high temperature data. From these results, long-term release of Kr were rredicted using an equation of the form:

$$\frac{d[Kr_R]}{dt} = Ae^{-AE/RT} [Kr] \quad (1)$$

FIGURE 5. Krypton Release Rate From Amorphous $\text{FeO}_{.79}\text{YO}_{.12}\text{KrO}_{.09}$

FIGURE 6. Krypton Release Rate From Amorphous $\text{FeO} \cdot 0.7\text{SrO} \cdot 0.06\text{KrO}$

where $\frac{d[\text{KrR}]}{dt}$ is the number of moles of Kr released as a function of time, A and ΔE are the rate parameters given in the figures, R is the gas constant in cal/mole-deg and T is the temperature in oK.

Since only release of ^{85}Kr is of concern, one must consider its radioactive decay in the solid matrix. The concentration of ^{85}Kr in the solid at a future time is obtained by integrating the differential equation

$$\frac{d[^{85}\text{Kr}]}{dt} = \lambda[^{85}\text{Kr}] + Ae^{-\Delta E/RT}[^{85}\text{Kr}] \quad (2)$$

to yield the equation

$$[^{85}\text{Kr}] = [^{85}\text{Kr}_0]e^{-kt} \quad (3)$$

where $^{85}\text{Kr}_0$ is the number of moles of ^{85}Kr in the solid at $t = 0$; $k = \lambda + Ae^{-\Delta E/RT}$, and $\lambda = 1.22 \times 10^{-7} \text{ min}^{-1}$. By combining equation (1) and (3) and integrating, the following expression results:

$$\frac{[^{85}\text{KrR}]}{[^{85}\text{Kr}_0]} = Ae^{-\Delta E/RT} \left[\frac{1}{k} - \frac{e^{-kt}}{k} \right] \quad (4)$$

Applying this expression to the data on gas release given in Figures 5 and 6 gives the results listed in Table IV.

TABLE IV. Long Term Release of ^{85}Kr From Amorphous Metal Deposits

	Fraction of ^{85}Kr Released in 100 Years 200°C	300°C	400°C
$\text{Fe}_{0.75}\text{Y}_{0.12}\text{Kr}_{0.08}$	1.1×10^{-5}	2.4×10^{-2}	8.5×10^{-1}
$\text{Fe}_{0.75}\text{Cr}_{0.19}\text{Kr}_{0.06}$	7.5×10^{-7}	6.6×10^{-4}	7.1×10^{-2}

Although more analyses will be required to confirm these results by actual long-term tests, and perhaps using ^{85}Kr in tracer quantities, it now appears that loss of ^{85}Kr will be negligible at temperature below 250°C for $\text{FeO}_{.79}\text{YO}_{.12}\text{KrO}_{.09}$ and below 300°C for $\text{FeO}_{.75}\text{ZrO}_{.19}\text{KrO}_{.06}$.

The mechanism of gas release from sputtered deposits is of interest to enable a more realistic model of release as a function of time and temperature. On the basis of a very preliminary observation for the crystalline metals, release appears to involve bubble formation and then bubble diffusion. Gas release from amorphous metals appears to be much more closely tied to the crystallization phenomenon. In the $\text{FeO}_{.79}\text{YO}_{.12}\text{KrO}_{.09}$ the sample actually disintegrates to a fine powder during the gas release process. Apparently, crystallization and/or gas release causes unusual strain in the lattice and fracture of the sample. This does not occur in the $\text{FeO}_{.75}\text{ZrO}_{.19}\text{KrO}_{.06}$ sample, but release of gas is probably still associated with crystallization **of the amorphous metal. The mechanism of gas release from these deposits is** being further investigated and will be the subject of subsequent papers.

ENGINEERING FEASIBILITY AND ECONOMIC ANALYSIS

At the present stage of development, any economic evaluation of the process for trapping Kr in sputter deposited metals must be considered no more than a preliminary indication. Nevertheless, it is useful to attempt such an evaluation at this point to provide guidance in comparing various techniques for ^{85}Kr storage and, thus, appropriately apply our resources to the most promising techniques. For this evaluation, we have somewhat arbitrarily selected a "reference process" as a basis for our cost estimates.

Brown, Knecht, and Thomas(18) have estimated that the ^{85}Kr yield from a plant reprocessing 2000 tonne/year of LWR fuel will be about 17 MCi/year. It has also been suggested that the total ^{85}Kr generated in reprocessing DOE defense nuclear fuels in the period from 1978 to 1989 will be about 20 MCI. In both cases, the ^{85}Kr will make up about 6% of the total Kr gas with possibly a few percent of non-radioactive Xe present. It is, therefore, necessary to develop a system capable of handling a total of about 850 kg of Kr

(225 m³ at STP) in the period from 1978 to 1989 for the defense waste or about 720 kg/year (190 m³ at STP) for a 2000 tonne/year commercial reprocessing plant.

Our evaluation of the engineering feasibility of the process is based upon a reference sputtering apparatus, which is scaled up by a factor of only 3.6 from our current laboratory apparatus. This system will produce a cylindrical deposit 56 cm long with an inside diameter of about 14 cm (Figure 7). The coating will be about 5.5 mm thick and of the approximate atomic composition Fe_{0.79}Y_{0.12}Kr_{0.09}. The film will be deposited on about 6.4 mm of copper (the substrate). As currently envisioned, the inside surface will be coated with a 0.1 mm layer (300 g) of defect-free nickel containing no ⁸⁵Kr. The necessity of this close-out layer has not been demonstrated, but is included in this evaluation. Such a layer may be beneficial in limiting corrosion, reducing gas release, and increasing mechanical stability of the storage unit. Each deposit will contain about 9.5 kg of the amorphous alloy of which 1.1 kg is Kr.

Based on this model, the estimated costs, excluding labor, are tabulated in Table IV.

TABLE IV (1): Estimated Costs of Sputter Deposition of Kr in Fe_{0.79}Y_{0.12}Kr_{0.09} (excluding labor)

Cost Item	Cost, \$1000 (1978 value)		
	100 hr Run	Annual Costs (2) for Defense Waste	Annual Cost for (3) Commercial Plant
Capital Equipment(4)	1.31	100	850
Electric Power (0.05/kWh)	0.37	30	240
Materials and Fabrication	1.26	100	830
Total	2.94	230	1920

(1) Detailed cost breakdown found in the appendix.

(2) ~2 MCi ⁸⁵Kr/year

(3) ~17 MCi ⁸⁵Kr/year

(4) 7 year depreciation schedule, 12% interest

FIGURE 7. Typical Sputtered Deposit for Krypton Storage

These costs do not include all of the costs, only those which are more easily separated from the waste handling function and which are unique to this technique. Perhaps the greater costs are the cost of the facility and the labor which appear to be similar for all potential storage techniques. The facility costs have not been estimated for this paper, but a sample sputtering layout is given in Figure 8 for the defense waste operation. The labor costs depend to a large extent in how the manpower is used in conjunction with the separations, and other waste handling processes. For the purposes of this paper, we have estimated a two-man operation with 80 hours/week at an annual labor and overhead cost of \$150,000/year. This should supply the labor requirements for the defense waste operation, but would not be sufficient for the commercial plant. It is anticipated that the commercial plant could operate with four to six full time employees.

In spite of the preliminary nature of these cost estimates, it does not appear that the cost of the sputtering technique should be limiting. The selection of the process should, therefore, be based on product quality and safety. It should be understood that the reference process discussed is a well proven system with scale-up of only 3-6 for commercial operation. Thus, the system as described is largely proven with our current laboratory scale experiments. In addition, the scale-up of the major components has been tested on a 2x scale already. Additional cost savings may be possible by a much larger scale-up factor for a commercial plant but our estimates are made on the basis of a concept which is largely proven at the present time.

FIGURE 8. High-Rate Sputtering/Ion Implantation Facility

CONCLUSIONS

The ability to trap relatively large quantities of gas during the sputter deposition of metals and metal alloys has been shown to be a viable technique for storage of radioactive gases from waste nuclear fuels. Sputtered deposits with from 3 to 5 atom% Kr have been prepared in Fe, Ni, Al, and Ti. A much larger Kr concentration has been trapped in sputtered amorphous metals with significantly less energy required. Several amorphous materials were investigated, all of which yield deposits containing from 5 to 12 atom% Kr. Alloys studied, which did not trap significant quantities of Kr, were shown by X-ray diffraction to be crystalline.

Kr release rates from the metal deposits were measured and found to be very low at temperatures below 300°C. In particular, release from the amorphous metals was below 10^{-7} %/minute below 300°C. These rates are sufficiently low for storage of ^{85}Kr without any significant contamination to the environment.

Preliminary estimates of the costs involved in the sputtering process indicate that equipment, power, and materials costs will not be limiting. Labor and facilities costs are not expected to be significantly different from those of other potential ^{85}Kr storage processes.

Scale up of the process to handle the quantities of ^{85}Kr expected to be generated in nuclear power fuels appears to be feasible and work is in progress to further evaluate this point. Additional questions yet to be evaluated include the influence of the decay product Rb and the effect of the radiation on both the process and the product.

At present, it appears that the sputtering process has excellent potential for storage of ^{85}Kr in a stable solid product without the possible safety hazards associated with processes which require extremely high pressures or high temperatures.

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APPENDIX

APPENDIX

DETAILS OF COST BREAKDOWN

Capital Eguipment (One Sputtering Unit 3.6 times larger than lab scale unit)

<u>Component</u>	<u>Cost, \$K</u>
Power Supplies	55
Arc-Current Limiters	25
Vacuum Station	25
Ion Implantation/Sputtering Chamber	50
Process Controls, Instrumentation and Microprocessor	57
Residual Gas Analyzer	22
Vacuum Leak Detector	12
Shield Processing Equipment	24
Subtotal	270
Equipment for "Hot Cell" Operation	130
Tota 1	400

Capital Equipment*
Cost per Deposition (100 hour run) 1.31

Materials Costs (For one 100 hour run)

<u>Materi a l</u>	<u>Cost, \$K</u>
Substrate Material (20" Cu pipe)	0.1
Target Material	0.5
Miscellaneous Materials	
Substrate Fabrication	
Target Fabrication	0.5
Miscellaneous Materials Fabrication	0.1
Total per Deposition	1.2
<u>Total per Year</u>	84

*Seven year depreciation schedule, 12% interest.

Power Requirements and Costs (For one 100 hour run)

<u>Component</u>	<u>Operating Condition</u>	<u>Power, kWh</u>	<u>Cost, \$</u>
Substrate	250 V (25 amp)	625	31
Target	2500 V (18 amp)	4300	215
Plasma	70 V (70 amp)	490	25
Filament Heat	10 V (56 amp) (6)	336	17
Target Limiter	$\Delta V = 300$ (18 amp)	540	27
Other Supplies and Limiters	10%	649	32
Process Control	120 V (25 amp)	300	15
Total:		7440	362

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