Development and Selection of a Matrix Alloy for ^{85}Kr Encapsulation

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SUMMARY

Pacific Northwest Laboratory (PNL) has developed and demonstrated a pilot-scale process for stable, long-term storage of radioactive ^{85}Kr gas from spent nuclear fuel. The process entraps the Kr into a solid metal matrix that can be safely stored at ambient pressure.

For this matrix numerous alloys were first screened; those that best satisfied the selection criteria were Cu-Y, Ni-Y, and Ni-La. Of these, Cu-Y alloys containing approximately 20 at.% Y were recommended for use in the pilot-scale system. Reasons for this decision, based on the development work described in Section 5, are summarized here.

Thick Cu-Y-Kr deposits (≥ 1 mm) exhibit much better thermal and mechanical stability than do those of Ni-La-Kr and are at least as stable as Ni-Y-Kr deposits. Cu-Y-Kr coatings are very compatible with the sputtering process. They adhere well to the substrate, do not spall significantly during deposition, and can be deposited at higher rates than the Ni-base alloys. This faster deposition helps compensate, in terms of process efficiency, for the lower Kr capacity of Cu-Y-Kr alloys. Another advantage of Cu-Y over Ni-base alloys is the higher vapor pressure of Cu compared to Ni. This reduces the unwanted buildup of Cu on the hot anode surface, whereas deposition of Ni is a problem with Ni-Y, for example.

Cu-Y-Kr deposits containing 17 to 20 at.% Y and 6 to 8 at.% Kr compared favorably to $\text{Ni}_{80}\text{La}_{10}\text{Kr}_{10}$ in terms of long-term Kr retention characteristics. The measurements of Cu-Y-Kr by differential scanning calorimetry also indicated stable retention of Kr because rapid release did not occur below $\sim 650^\circ\text{C}$. Finally, Cu-Y alloys are satisfactory in terms of materials costs and producibility of the sputtering target.

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DEVELOPMENT AND SELECTION OF A MATRIX ALLOY FOR ^{85}Kr ENCAPSULATION

1.0 INTRODUCTION

Under direction of the U.S. Department of Energy, PNL has developed and demonstrated a pilot-scale process for stable, long-term storage of radioactive ^{85}Kr gas which is released from spent nuclear fuel.⁽¹⁻³⁾ As an alternative to high-pressure compressed gas storage, the PNL process entraps the Kr within a solid metal matrix that can be stored safely at ambient pressure. Krypton gas is incorporated into a solid matrix using a high-rate bias sputtering process. The gas is ionized and is implanted into a growing, sputter-deposited metal, which is ultimately built up to a thickness of about 1 cm.

A major requirement of this program was to develop a metallic matrix material compatible with process and storage needs. The implantation process selected demanded a material capable of stably entrapping high concentrations (>6 at.%) of Kr using implantation energies of a few hundred electron volts. At the start of this program, little data existed on the basic properties and stability of Kr-loaded bulk alloys of the type compatible with the selected process. Bulk metal alloys containing concentrations of inert gas greater than the parts per million level had not been produced or studied because of the special nonequilibrium methods required in their production. Some studies had dealt with thin gas-implanted layers in metals.⁽⁴⁻⁶⁾ Ongoing European studies on gas-implanted bulk deposits focused on pure metals not applicable to the PNL process.⁽⁷⁻⁹⁾ Therefore experiments to screen alloys were planned and performed that used a small-scale apparatus to implant nonradioactive Kr and allowed small quantities (10-100 grams) of alloys to be produced and evaluated.

Although some results of these experiments have been reported previously,^(10,11) this report summarizes the experiments in alloy development that led to selection of a Cu-Y-Kr alloy for pilot plant demonstration runs. Rather than provide details on individual alloy behavior, the purpose of this

report is to explain the methods of alloy selection and to provide information on alloy performance as it relates to the selection criteria.

The following section lists and discusses criteria used to evaluate alloy performance. The rationale for focusing this work on transition metal/rare earth alloys is then discussed. Next is a brief description of the experimental methods and apparatus used to produce and characterize the alloys. Experimental results are then presented and discussed. A final section discusses the reasons for selecting the Cu-Y-Kr alloys as the pilot-plant matrix material.

2.0 ALLOY PERFORMANCE CRITERIA

The alloy selected as the matrix material for storage of ^{85}Kr must satisfy physical and economic requirements of the implantation process and must provide safe and stable long-term containment of the radioactive gas. Listed below are the criteria used to evaluate the various candidate alloys, followed by a discussion of each item. The alloy selection process is also pictured as a flow chart in Figure 1.

1. Kr release rate within regulatory limits at storage temperature
2. acceptable mechanical and metallurgical stability during deposition and during storage
3. compatibility with high-rate sputter deposition process
4. capability to incorporate high Kr concentrations (≥ 6 at.%) using low energy implantation process
5. moderate cost for raw material and for sputtering target fabrication.

Long-term containment of the ^{85}Kr at storage temperatures is the primary requirement of the matrix alloy. A material's capability for containing Kr depends on its mechanical integrity and on low diffusivity of Kr in the material. Studies have shown that sputter-entrapped Kr is retained atomically within the matrix or in micro-bubbles smaller than 3 nm diameter.⁽⁷⁾ Gas release occurs when a Kr atom diffuses to a free surface or crack, or when a crack intersects a Kr bubble. A material permeated by microcracks or divided into fine particles provides short diffusion paths for escape of the Kr. Therefore, minimum Kr release occurs in a material with high mechanical integrity (few cracks) and with a low Kr diffusion coefficient.

The second criterion, mechanical and metallurgical stability, is necessary for successful deposition of the alloy as well as for long-term containment of Kr. Both the deposit and the deposit/substrate composite must remain intact. Mechanical failure occurs when the deposit debonds from the substrate or breaks apart, or when flakes or particles spall from the deposit because of internal stress. Occurrence of any of these events during deposition interrupts the process. For example, metallic flakes and particles can cause excessive plasma

FIGURE 1. Flow Diagram Showing Procedure Used To Select and Evaluate Matrix Alloys for ^{85}Kr Implantation and Encapsulation

ancing or can create electrical short-circuits that terminate the trapping. If debonding or delamination occurs during deposition, transfer of heat to the substrate is greatly reduced, and the Kr trapping rate is reduced in proportion to the area affected. Metallurgical stability refers mainly to the absence of unwanted phase transformations, which might, for example, produce volume changes that cause debonding or fracturing.

The importance of alloy mechanical integrity in minimizing pathways for Kr diffusion and release was mentioned above. A second way that mechanical discontinuities could accelerate Kr release results from the radioactive decay heat of ^{85}Kr . Debonded or isolated regions of deposit will become thermally hotter than regions in contact with the substrate. Hot regions will release Kr at a higher rate because of increased diffusivity of the Kr.

The third criterion addresses the need to satisfy some minimum processing rate (Kr entrapment rate) of the plant, since Kr consumption is proportional to the alloy's deposition rate. Not all conductive materials can be readily direct-current sputtered at high rates. Some have a low sputtering yield, while others have poor thermal conductivity, high vapor pressure, or thermo-mechanical instabilities that prevent the targets and substrate/deposits from accepting the heat loads imposed by the high-rate sputtering process.

The fourth criterion relates to the gas-trapping efficiency of the deposit. In the entrapment process, positively charged Kr ions are accelerated toward the negatively biased deposit surface. Krypton atoms that adhere to the surface become buried by freshly deposited metal. The fraction of impinging ions that adhere to or become buried in the surface is the Kr^+ sticking coefficient. This coefficient depends strongly on ion energy and target material, and it typically peaks at energies less than several hundred electron volts. The relative importance of the sticking coefficient depends on the substrate-biasing mode used in the implantation process.^(10,12) Here, a process-related decision was made to use a low-voltage dc substrate bias to reduce operating costs. Thus the sticking coefficient of the matrix material must be very high to obtain entrapped Kr concentrations of 6 to 10 at.%.

Economy dictates the final criterion. Materials with high intrinsic cost, e.g., precious metals and certain rare earths, were ruled out because of the relatively large quantities of matrix material consumed. A commercial-scale plant capable of reprocessing 2000 MTHM/yr could use 1500 kg of rare earth per year.⁽³⁾ Another economic factor was amenability to standard methods for fabrication of the sputtering-target.

3.0 PRELIMINARY SELECTION OF TRANSITION METAL/RARE EARTH ALLOYS

As alluded to earlier, a programmatic decision was made to operate the Kr implantation process in a low-energy, steady-state direct-current mode rather than in a high-energy pulsed mode. In the latter process, which is being developed in the U.K. by Whitmell and coworkers,⁽⁷⁻⁹⁾ Kr ions are implanted at an energy of about 6 keV. Pure metal matrix materials can be used because the ions are implanted below the atomic surface layer and thus the Kr sticking coefficient is relatively insensitive to material. In contrast, one major limitation of the low-energy direct-current process is that Kr ions of a few hundred electron volts will not penetrate and become entrapped in the surface of most metals and alloys. Such low-energy ions are reflected back into the plasma, or they reside only briefly on the surface before being emitted.

The low-energy direct-current process for implementing Kr, however, is feasible using certain classes of alloys, such as transition metal/rare earth alloys (TM/RE), which have an unusually high sticking coefficient for inert gases.⁽¹⁰⁾ A study published in 1977 by Cuomo and Gambino⁽⁴⁾ at IBM showed that large concentrations of inert gases (e.g., 13% Kr) could be incorporated into bias-sputtered thin films of CoGd and CoGdMo. Subsequent experiments at PNL by McClanahan et al.⁽¹⁰⁾ showed that Kr concentrations up to 9 at.% could be incorporated into various TM/RE thin film and thick film alloys produced by high-rate direct-current bias sputter deposition. Much lower Kr concentrations (<1%) were entrapped in pure metals and in several other alloys produced by the same process.

As a result of these findings and based on the five criteria listed in Section 2, selection of a matrix material centered on the TM/RE alloys. Nickel and copper were given prime consideration as the transition metal component because of their environmental stability, relatively low cost, good machinability, and compatibility with the sputtering process. Iron-based alloys also were considered, but were rejected because of the high oxidation rate (rusting) of iron. For the minor alloy constituent, the lighter rare earths (La, Ce) and yttrium were the main contenders, in part because of their low cost. Because experimental evidence suggested that the high Kr sticking coefficient of the

TM/RE alloys was due partly to the large atomic size ratio of the RE atoms,^(10,11) several non-rare-earth metals of large atomic size were also tested.

4.0 ALLOY PRODUCTION AND EVALUATION

4.1 SPUTTER DEPOSITION SYSTEM

Alloy screening experiments were performed in a bench-scale Kr implantation apparatus designed much like the larger pilot-plant equipment.^(a) The Kr-loaded alloys were produced in a small cylindrical vessel that served both as the substrate and the vacuum chamber. Alloys were deposited directly onto the water-cooled chamber wall. Two somewhat different substrate designs were used. The initial design was a 7.3 cm ID by 10 cm long, thick-walled pipe of copper or aluminum with a deposit surface area of $\sim 230 \text{ cm}^2$. An improved design was a stainless steel pipe 7.8 cm ID by 13 cm long, with an ellipsoid endcap, and with a total deposit surface area of $\sim 345 \text{ cm}^2$. The latter design, shown in the line drawing of Figure 2, is a replica of the pilot-plant-scale chamber.

In either design, the substrate surrounded and was concentric with the cylindrical sputtering target. The substrate was water-cooled by use of an external water jacket to keep the substrate/deposit $\sim 25^\circ\text{C}$. It was electrically isolated from ground so it could be negatively biased with a voltage corresponding to the desired energy for ion implantation. The interior was pumped with a throttled, cryotrapped diffusion pump that provided a base pressure of $6 \times 10^{-5} \text{ Pa}$. The Kr plasma discharge, produced with high-purity, research-grade Kr, was thermionically supported by electrons emitted from a tungsten filament located above the target/substrate assembly. Inflow of Kr during deposition was regulated by a feedback loop consisting of a variable leak valve, a capacitance manometer, and control circuit, to maintain a reference pressure of 0.5 Pa ($4 \times 10^{-3} \text{ torr}$) near the chamber inlet. Instantaneous readout of the Kr entrapment rate during processing was obtained by monitoring the net inflow of Kr to the chamber. All pertinent processing parameters were recorded on strip-chart recorders or by computer data loggers.

(a) E. D. McClanahan, R. W. Moss, and E. N. Greenwell. "Operation and Control of an Ion-Implantation/Sputtering Storage Device for ^{85}Kr ." PNL-SA-13239, submitted for publication in J. Vac. Sci. Technol., Series A, January 1986.

FIGURE 2. Cross-sectional Schematic of High-rate Sputter Deposition/Kr Ion Implantation Apparatus Used in Bench-scale Alloy Development Experiments

The cylindrical sputtering targets, machined from Ni-200 or OFHC Cu bar stock, contained inserts of the alloying element(s) (La, Y, etc.), which had been pressed into drilled holes or slots. Purity of the metals was at least 99.9 at.%. Targets were water-cooled via an internal cooling channel. Targets used in the initial system design were 2.54 cm dia by 11.4 cm long and contained pellet-like inserts. In the improved design, targets were 3.8 cm dia by 11.5 cm long, and contained annular ring-shaped inserts. With this design, a larger fraction of the target surface could be occupied by the alloying element(s), and thicker deposits could be made.

In some experiments, a wide range of alloy compositions was obtained in a single run for screening purposes by using a compositionally nonuniform target. Here, the average alloy composition varied along the axial direction by varying the insert size and spacing. Correspondingly, the concentration of alloying element (e.g., La or Y) varied by as much as 23 at.% along the length of the substrate. Kr content versus alloy composition could be quickly evaluated in this manner.

4.2 PROCESS PARAMETERS AND EXPERIMENTAL PROCEDURE

Process parameters typically used during steady-state deposition of alloys are listed in Table 1. A special startup procedure was performed before steady-state alloy deposition and Kr trapping were achieved. After the baseline Kr flow was adjusted, the plasma was ignited and the substrate surface was sputter-cleaned at ~100V and 60 A/m² for ~10 min to improve bonding. Material sputtered from the target was deposited onto the unbiased target, and was subsequently redeposited onto the substrate when target voltage was increased to begin steady-state deposition.

The substrate bias voltage was adjusted at the beginning of steady-state deposition to maximize Kr trapping. Optimum bias voltage was about 225 V for many alloys tested. A run was terminated either when the scheduled time was reached, or because of equipment failure.

TABLE 1. Process Parameters

Target Bias Voltage	2400 V
Target Current Density	100-120 A/m
Substrate Bias Voltage	220-270 V
Substrate Bias Current	80-90 A/m ²
Plasma Voltage	45-60 V
Plasma Current	4 A
Chamber Pressure	0.53 Pa (4 millitorr)
Kr Inflow (baseline)	1 sccm
Kr Inflow (total during typical run)	3-4 sccm

4.3 ALLOY EVALUATION METHODS

The principal materials properties or phenomena measured during these experiments are described below. Only the instantaneous Kr trapping rate was measured in situ. Other measurements were performed on sections of deposit cut from the cylindrical substrate.

Kr Trapping Rate

The instantaneous Kr trapping rate was monitored using an inline flow-meter. The instantaneous flow rate provided only an approximate measure of the entrapped Kr concentration, which depended also on the metal deposition rate. However, net Kr flow rate integrated over the duration of the run yielded the total volume (or moles) of entrapped Kr. This value, divided by total deposit mass, yielded the average Kr content of the alloy.

Kr Concentration in Alloy

Concentration was measured directly using two different methods: 1) vacuum fusion with gas chromatography and 2) energy dispersive spectroscopy (EDS) in a scanning electron microscope (SEM). In the first method, a small deposit sample (<20 mg) was heated to melting in an evacuated quartz tube. The identity and volume fractions of released gas were measured by gas chromatography. Most measurements of Kr content, however, were made by EDS because of the method's convenience. Metallic alloy composition was also measured by

EDS. EDS measurements of Kr content were calibrated against standards whose gas content was determined by the vacuum fusion method.

Kr Release Rate

Extensive measurements of Kr release rate were performed by sealing specimens in evacuated quartz ampules and holding them at constant temperature for various time periods. Gas chromatography was used to measure Kr released into the ampule. Gas release could also be monitored almost continuously by heating samples in a chamber from which Kr was collected periodically and measured using a gas chromatograph. Samples were measured in two ways: 1) isothermally at temperatures ranging from 250 to 500°C, generally for 5 to 30 days and 2) at a constant heating rate of 4°C/min from 20°C to 1300°C and then held at 1300°C until gas release was complete. Further details on gas release measurements are given by Lytle et al. (2,a)

Thermal Stability

Stability of the alloys relative to rapid gas release and solid-state phase transformations was judged by several methods. Approximate temperatures for Kr release and phase transformations (e.g., amorphous + crystalline) were measured by differential scanning calorimetry (DSC) and differential gravimetric analysis (DGA), at constant heating rates to maxima of about 750°C. Gas release temperatures were estimated also by heating specimens in a quartz tube vacuum furnace while monitoring chamber pressure with an ionization gauge. Rapid Kr release resulted in pressure bursts several orders of magnitude higher than the system's base pressure.

Alloy Structure and Microstructure

The crystalline state of each deposit was determined by x-ray diffraction (XRD) using an automated diffractometer. The microstructure of selected alloys was examined by SEM and by transmission electron microscopy (TEM) to evaluate characteristics such as porosity, homogeneity, and existence of gas bubbles.

(a) J. M. Lytle, G. L. Tingey, and E. D. McClanahan. "Dependence of Krypton Diffusion Kinetics on Solid State Structure in a $\text{Ni}_{81}\text{La}_9\text{Kr}_{10}$ Alloy," submitted to J. Phys. Chem.

Mechanical Stability

The mechanical stability of each alloy was evaluated qualitatively by watching for direct and indirect evidence of deposit peeling and spalling. Unstable behavior during deposition was generally reflected in process instabilities or failure, for example, plasma arcing or short circuits. Peeling and spalling were detected visually after deposition when the chamber was opened for inspection. Hidden defects such as poor substrate and/or deposit bonding were often revealed when the deposit/substrate was sectioned to obtain specimens for compositional and structural analysis.

5.0 ALLOY PERFORMANCE

This section describes the characteristics and behavior of various alloys that were investigated for use as the Kr storage matrix. As explained in Section 3, most of the materials are transition metal-rare earth binary alloys. Table 2 identifies the alloy composition ranges, entrapped Kr concentrations, and substrate bias voltages (Kr ion implantation energies) used during deposition.

Instead of providing a detailed account of the behavior of each alloy, results are discussed in terms of the criteria outlined in Section 2. Because the goal of this program was to develop a workable matrix alloy on schedule and within budget rather than to perform systematic basic research, certain alloys were investigated much more thoroughly than others. Alloys that displayed good Kr trapping characteristics and stability during initial screening were given the greatest attention. For example, Ni-La alloys were among the first alloys investigated, and were found to possess a promising combination of properties. They continued to be investigated for several years, until it became evident that mechanical instability prevented the formation of thick deposits. Therefore, much more data was collected on Ni-La than on alloys such as Ni-U or Cu-La, which behaved poorly during screening.

5.1 COMPATIBILITY WITH DEPOSITION PROCESS

All alloys listed in Table 2 could be readily sputtered to produce thin coatings (≤ 0.2 mm). For cost effectiveness, however, coatings as thick as 1 cm were desired to contain as much Kr as possible per unit. Differences among the alloys became more apparent when producing thick deposits, which required long run times. Problems encountered that could be related directly to the matrix alloy included 1) spalling of flakes and particles from the substrate, from the deposit itself, or from other surfaces within the chamber; 2) accumulation on nonsubstrate surfaces; and 3) excessive plasma arcing. Metallic particles and flakes, and accumulation of deposit on electrode surfaces, can create electrical shorts or arcs within the apparatus. Excessive arcing in itself can create instabilities in gas flow and pressure that reduce the efficiency of deposition and gas entrapment.

TABLE 2. Composition and Kr Content of Candidate Matrix Alloys

Target Material	Run No.	Minor Metal Comp, at. %	Deposit Kr Content, at. %	Substrate Bias (V)	Comments
Ni-La	GT98	10.0	10.0	-225	
Ni-La	GT102	12.1	10.0	-227	
Ni-La	GT104	12.2	3.3	-95	Sub-optimum bias
Ni-La	GT108	0.30-	0-	-225	Variable composition
		22.9	14.7		
Ni-La	GT110	0.30-	0-	-175	Variable composition
		22.4	14.4		
Ni-La	GT131	Not Measurable	Not Measurable	-225	Substrate heated to 90°C during deposition
Ni-Ce	GT-95	9.9	5.4	-225	
Ni-Ti	GT-99	38	2.4	-225	
Ni-U	GT-100	28	1.0	-250	
Ni-La-Mo	GT-105	8.4% La 18.0% Mo	5.4	-175	
Ni-Y	GT-126	3.2-	0.6-	-225	Variable composition
		17.8	7.9		
Fe-Y	--	9.0	9.0	-225	
Cu-La	GT-130	3.2-	0.6-	-225	Variable composition
		24.5	5.9		
Cu-Y	GT-129	3.0-	0.80-	-225	Variable composition
		16.4	6.9		
Cu-Y	GT-137	18.5	8.6	-270	
Cu-Y	GT-142	2.0-	1.0-	-270	Variable composition
		16.5	7.1		
Co-Gd-Mo	GT-119	31% Gd 11% Mo	7.4	-135	

Although only a qualitative evaluation could be made, Cu-Y alloys exhibited the best behavior of the several alloys selected for producing thick (>1 mm) deposits. Cu-Y adhered well to foreign surfaces and to pre-existing Cu-Y surfaces so that little spalling occurred, and it could be sputtered with little arcing. Ni-Y alloys also behaved well, but the Cu-Y alloys had the advantage of a higher vapor pressure and thus less metal accumulated on the hot anode surface above the target. This surface could not be completely shielded from the sputtered flux; therefore accumulation of deposit on it without re-evaporation eventually caused a short circuit to the target or substrate.

Alloys of La with Cu or Ni were not as compatible with the sputtering process as the corresponding Y alloys. Frequent plasma arcing occurred during deposition, which sometimes required a 30% reduction in target bias voltage to maintain stable operation. The chief limitation of these alloys was mechanical instability in thick (≥ 1 mm) deposits, which is discussed more fully below. Flakes and particles of deposit, which debonded from the deposit itself, created electrical short circuits that terminated operation of the system.

5.2 Kr TRAPPING CAPABILITY

For a given base metal (e.g., Ni or Cu), the concentration of Kr incorporated into the alloy deposit depended strongly on the type and concentration of alloying element, and on the substrate bias voltage (Kr ion implantation energy) used during deposition. The effect of elevated substrate temperature was also examined in one experiment (GT131).

Table 2 indicates the variation in entrapped Kr concentration with the type and concentration of alloying element. No simple relation between the type of alloying element and the entrapped Kr content could be discerned, except that large atoms such as La, Ce, and Y were more effective than small atoms. The highest Kr concentrations were found in Ni-La alloys, which entrapped as much as 14 at.% Kr at La concentrations of 20 to 22 at.%. Ni-Y and Cu-Y alloys trapped as much as 8 at.% Kr. A Ni-La-Mo ternary alloy was tested in experiment GT105, but the presence of Mo did not increase the Kr

capacity. The Ni-U alloy tested in experiment GT100 contradicted the "large atom" hypothesis, in that only 1 at.% Kr was entrapped in that experiment.

The effect of alloy composition on incorporation of Kr was studied systematically for Ni-La-Kr, Ni-Y-Kr, and Cu-Y-Kr alloys using variable-composition sputtering targets. Here, the rare earth concentration in the deposit varied from nearly zero at one end of the cylindrical substrate to 20-30 at.% at the other end. Substrate bias voltage was necessarily kept constant during a run, and was optimized for rare-earth concentrations of about 10 to 15 at.%.

Figures 3a and 3b show the concentration of entrapped Kr as a function of La concentration for Ni-La-Kr alloys deposited at substrate bias voltages of -225V and -175V, respectively (experiments GT108 and GT110). At the higher bias, Kr content initially rises slowly with La content, then increases rapidly at a linear rate between 5 and 15 at.% La. Kr content saturates quickly above 15 at.% La, reaching a maximum of ~13 at.% Kr at ~25 at.% La. At -175V bias (Figure 3b), Kr concentration does not rise as rapidly with La in the 5 to 15 at.% La interval, and saturation occurs more gradually. Figures 4a and 4b show the effect of Y content on entrapped Kr concentration for Ni-Y-Kr alloys deposited with -225V substrate bias. Behavior is much like that of Ni-La-Kr, except that the maximum Kr content reaches only 7.5-8 at.%. Kr trapping behavior for Cu-Y-Kr alloys deposited at -225V and -270V substrate bias is shown in Figure 5. The GT137 data point was obtained from a single composition $\text{Cu}_{74}\text{Y}_{18}\text{Kr}_8$ deposit. Again, Kr content rises monotonically with Y, then saturates above ~15 at.% Y. As with the Ni-La-Kr alloys, a higher substrate bias yields a higher Kr concentration over most of the rare-earth composition range.

5.3 MECHANICAL AND METALLURGICAL STABILITY

Mechanical Stability

All Kr-loaded alloy deposits were brittle and contained high compressive stresses. In some alloys, these characteristics caused spalling and debonding during deposition, which, as discussed in Section 5.1, could impede or terminate the deposition process. Adherence between deposit and substrate was usually strong because of the substrate cleaning (sputter etching) done before

FIGURE 3. Implanted Kr Concentration Versus La/Ni Ratio in Ni-La-Kr Alloys Deposited at Substrate Bias Voltage of a) -225V and b) -175V

FIGURE 4. Implanted Kr Concentration Versus Y Content in Ni-Y-Kr Alloys Deposited at Substrate Bias Voltage of -225V: a) over Composition Range of 3-18 at.% Y; b) Detailed Measurement over Composition Range of 3-10 at.% Y

FIGURE 5. Implanted Kr Concentration Versus Y Content in Cu-Y-Kr Alloys Deposited at Two Different Substrate Bias Voltages. Experiment GT137 was conducted using a single-composition Cu-Y target.

the alloy was deposited. Specific problems related to mechanical stability that were encountered during deposition included the following:

- Debonding and peeling of freshly deposited layers from an existing layer of TM/RE/Kr deposit. This could occur after a run was interrupted because of an equipment problem, allowing contamination or alteration of the deposit surface. Although this surface was typically sputter-etched before resuming deposition, the resulting interface was weaker than the bulk deposit.
- Spalling of small, nearly hemispherical chunks (0.5-3 mm dia.) from the deposit surface, leaving craters or pockmarks behind. This behavior was apparently caused by the high compressive stress and brittle nature of the material.

- Debonding from nonsubstrate surfaces, e.g., from the anode ring located above the target.

The practical test of mechanical stability was the successful production of thick (≥ 3 mm) deposits. Once formed, such deposits were stable except for some macroscopic cracking. Thick deposits of Cu-Y-Kr and Ni-Y-Kr containing 10 to 20 at.% Y were successfully produced. While the Ni-Y-Kr alloys were satisfactory, the Cu-Y-Kr alloys exhibited less peeling and spalling during deposition. Ni-La-Kr deposits containing 10 to 20 at.% La and 8 to 10 at.% Kr spalled and peeled badly when thickness exceeded approximately 1 mm, so that bulk deposits could not be made.

Several techniques aimed at reducing internal stress were tested in order to improve the deposit's mechanical integrity. In experiment GT131, the substrate was heated to 90°C during deposition to relieve stress in a Cu-La-Kr deposit. Heating, however, actually caused more severe peeling than was present in a substrate at room temperature. For various deposits, a gridlike pattern of grooves ~ 1 mm deep and spaced 1/2-1 cm apart was cut into the substrates to accommodate expansion of the deposit due to compressive stresses. These grooves did seem to arrest the growth of macroscopic cracks, but did not alleviate the fine-scale peeling and spalling in deposits such as Ni-La-Kr.

Metallurgical Stability

Destructive phase transformations, severe corrosion (oxidation), or other metallurgical instabilities were generally not encountered in TM-RE-Kr alloys evaluated here. The spalling and peeling observed in materials such as Ni-La-Kr during deposition presumably resulted from buildup of mechanical forces (stresses) rather than from phase transformations.

All TM-RE-Kr alloys underwent an amorphous-to-crystalline phase transformation during heating. It is important to note that this transformation was not mechanically destructive and did not cause catastrophic release of Kr from bulk deposits, although it did affect diffusivity of the Kr.^(a) As-deposited

(a) J. M. Lytle, G. L. Tingey, and E. D. McClanahan. "Dependence of Krypton Diffusion Kinetics on Solid State Structure in a Ni₈₁La₉Kr₁₀ Alloy," submitted to J. Phys. Chem.

alloys were fully or partially amorphous, depending on their Kr and RE content,⁽¹¹⁾ and they remained so until heated to their crystallization temperature. X-ray diffraction patterns in Figure 6 show how alloy structure varies with composition. The structure changes from a crystalline Ni/amorphous Ni-La-Kr mixture for $\text{Ni}_{91}\text{La}_5\text{Kr}_4$, to a fully amorphous deposit for $\text{Ni}_{70}\text{La}_{18}\text{Kr}_{12}$. Cu-Y-Kr and Ni-Y-Kr alloys behaved similarly. All were stable at room temperature and crystallized at temperatures ranging from 200 to 400°C. Some materials such as certain Ni-La-Kr alloys⁽¹³⁾ crystallized to a metastable structure, then transformed to the equilibrium crystal structure at higher temperatures. X-ray diffraction scans in Figure 7 illustrate these successive phase transformations during annealing of a $\text{Ni}_{90}\text{La}_{10}$ alloy. A differential scanning calorimeter (DSC) plot in Figure 8a for $\text{Ni}_{80}\text{Y}_{15}\text{Kr}_6$ reveals a crystallization temperature of ~390°C for this alloy (20°C/min heating rate). The irregularly shaped exotherm at 580 to 630°C is produced by rapid release of Kr, accompanied by fracturing and spalling of the alloy. Note that crystallization occurs at a distinctly lower temperature than does rapid Kr release. This behavior is discussed further in the next section.

Oxidation in air or in contact with moisture appeared to be a serious problem only with the Fe-Y-Kr deposits, which rusted. Other materials such as Ni-La-Kr and Cu-Y-Kr developed a surface tarnish after several days in air, but no bulk deterioration was apparent even after several years.

5.4 Kr RELEASE BEHAVIOR

Release of Kr from solid RE-TM-Kr alloys occurred in two distinct ways, depending on alloy temperature and Kr content. At moderate temperatures (e.g., $\leq 500^\circ\text{C}$ for $\text{Ni}_{80}\text{La}_{10}\text{Kr}_{10}$), Kr diffused out at a slow, continuous rate that increased exponentially with temperature,^(2,a) with little apparent macroscopic change in the alloy. At some higher temperature, in alloys containing more than ~3 at.% Kr, gas release occurred quickly in bursts, and was accompanied by fracturing and spalling of the deposit. The temperature at which rapid release

(a) J. M. Lytle, G. L. Tingey, and E. D. McClanahan. "Dependence of Krypton Diffusion Kinetics on Solid State Structure in a $\text{Ni}_{81}\text{La}_9\text{Kr}_{10}$ Alloy," submitted to J. Phys. Chem.

FIGURE 6. X-ray Diffractometer Plots for Ni-La-Kr Deposits Containing 0.6 to 22 at.% La and 0 to 13 at.% Kr. The deposits become increasingly amorphous as La and Kr content increases.

FIGURE 7. X-ray Diffractometer Plots Showing the Annealing Behavior of an Amorphous $\text{Ni}_{90}\text{La}_{10}$ Alloy. Annealing at 350°C causes crystallization to a non-equilibrium bcc crystal structure. This structure transforms to the equilibrium Ni_5La hexagonal phase during annealing at 650°C.

began depended on the heating rate. Alloys containing low (≤ 3 at.%) Kr concentrations did not exhibit rapid release behavior, presumably because high compressive stresses necessary for mechanical breakup were absent.

The most extensive measurements of diffusional Kr release characteristics were carried out on Ni-La-Kr alloys. Much of this work has been summarized by Lytle et al.^(a) The most important result in selection of the alloy is that Kr-loaded alloys are very stable at temperatures likely to be encountered during storage ($< 350^\circ\text{C}$). Lytle's work^(a) predicted that less than 0.5% of the Kr in $\text{Ni}_{80}\text{La}_{10}\text{Kr}_{10}$ would be released over the initial 10 years even at the maximum storage temperature of 350°C .

Measurements of the onset of rapid Kr release during heat-up at rates $\geq 4^\circ\text{C}/\text{min}$ were used to estimate deposit stability. While no definite relation was established between the rapid Kr release temperature and diffusional release characteristics at lower temperatures, these measurements at least verified the absence of rapid release at temperatures below about 300°C for all alloys tested. Referring again to the DSC scan (Figure 8a) of $\text{Ni}_{80}\text{La}_{10}\text{Kr}_{10}$ described briefly in the previous section, rapid Kr release begins at 590°C with a sharp, narrow exotherm, followed by a broader exotherm at 630°C . During this time the metal fractures into small (1 to 5 mm) pieces, each of them permeated by smaller fissures. The differential gravimetric (DGA) scan in Figure 8b verifies weight loss due to Kr release: about 9% of the initial sample weight is lost between temperatures of 590 to 630°C . As another example, Figure 9 shows a DSC scan of $\text{Cu}_{79}\text{Y}_{15}\text{Kr}_6$ at the same heating rate of $20^\circ\text{C}/\text{min}$. Rapid Kr release begins at 650°C , well above the crystalline transformation at 350°C .

Rapid Kr release temperatures for Cu-Y-Kr and Ni-La-Kr alloys heated at two different rates are listed in Table 3. Alloy thermal stability decreases with increasing Kr content. For example, Ni-La alloys containing 10 at.% Kr begin rapid release at a temperature $\sim 130^\circ\text{C}$ higher than alloys containing 13 at.% Kr. The release temperature increases with increased heating rate, as expected from reaction rate kinetics.

(a) J. M. Lytle, G. L. Tingey, and E. D. McClanahan. "Dependence of Krypton Diffusion Kinetics on Solid State Structure in a $\text{Ni}_{81}\text{La}_9\text{Kr}_{10}$ Alloy," submitted to J. Phys. Chem.

FIGURE 8. Differential Scanning Calorimetry (a) and Thermal Gravimetric Analysis (b) of $\text{Ni}_{80}\text{La}_{10}\text{Kr}_{10}$ deposit. In (a) the 400°C exotherm results from recrystallization while the 600°C exotherm results from rapid Kr release. The decrease in specimen weight caused by Kr release is shown in (b).

FIGURE 9. Differential Scanning Calorimetry Analysis of $\text{Cu}_{79}\text{Y}_{15}\text{Kr}_6$ Deposit. Recrystallization begins at about 340°C, and rapid Kr release begins at 650°C.

TABLE 3. Onset Temperature for Rapid Kr Release in
TM-RE-Kr Deposits Heated at Various Rates

<u>Deposit Material</u>	<u>Heating Rate, °C/min</u>	<u>Onset Temp, °C</u>
Cu ₇₈ Y ₁₅ Kr ₆	20	650
Cu ₈₁ Y _{13.5} Kr _{5.5}	20	670
Cu ₈₁ Y _{8.5} Kr _{3.5}	20	>700
Ni ₆₅ La ₂₂ Kr ₁₃	20	460
Ni ₇₂ La ₁₆ Kr ₁₂	20	490
Ni _{75.5} La ₁₃ Kr _{11.5}	20	510
Ni ₈₀ La ₁₀ Kr ₁₀	20	590
Ni ₈₀ La ₁₀ Kr ₁₀	7	500
Ni ₈₅ La ₁₂ Kr ₃	7	750

5.5 MATERIALS COSTS

Table 4 compares the relative costs of various elemental raw materials considered as potential matrix alloy components. Costs are based on material forms (e.g., forged bar) needed for fabrication of the sputtering target. Among the transition metals considered, Fe is by far the least expensive, but was ruled out because of oxidation. Co is nearly an order of magnitude more expensive than Ni or Cu. The few Co-base deposits made did not have outstanding properties, and, furthermore, Co is more difficult to fabricate into targets than are the other materials. The cost difference between Ni and Cu is relatively small, and did not influence the final selection of Cu alloys. Materials costs had a greater influence on selection of the rare-earth component. Elements such as Pr and Sm were ruled out mainly because of their high cost.

TABLE 4. Comparative Costs for Various Elemental Raw Materials
Considered as Potential Matrix Alloy Components

<u>Material</u>	<u>Type/Form</u>	<u>Cost, \$/kg</u>
Ni	B160-201, forged bar	40
Cu	OFHC, C101 forged bar	27
Fe	A108, cold rolled bar	2
Co	99.9% pure, forged bar	300
Y	99.9% pure, vac.-cast rod	430
La	99.9% pure, vac.-cast rod	240
Ce	99.9% pure, vac.-cast rod	250
Pr	99.9% pure, vac.-cast rod	1320
Sm	99.9% pure, vac.-cast rod	1320
Gd	99.9% pure, vac.-cast rod	540

6.0 REFERENCES

1. G. L. Tingey, E. D. McClanahan, M. A. Bayne, W. J. Gray and C. A. Hinman. 1980. "Krypton-85 Storage in Solid Matrices." Scientific Basis for Nuclear Waste Management 2:361-8.
2. G. L. Tingey, E. D. McClanahan, J. M. Lytle, N. R. Gordon and R. W. Knoll. 1982. "Krypton 85 Storage in Sputter-Deposited Amorphous Metals." PNL-SA-10536, Pacific Northwest Laboratory, Richland, Washington.
3. Krypton Encapsulation Preconceptual Design. 1981. Prepared for U.S. Department of Energy by the Ralph M. Parsons Company. Report No. 6154-3-1.
4. J. J. Cuomo, and R. J. Gambino. 1977. "Incorporation of Rare Gases in Sputtered Amorphous Metal Films." J. Vac. Sci. Technol. 14(1):152.
5. G. Carter, D. G. Armour, S. E. Donnelly, D. C. Ingram and R. P. Webb. 1980. "The Injection of Inert Gas Ions into Solids: Their Trapping and Escape." Radiation Effects 53:143.
6. R. Blackburn. 1966. "Inert Gases in Metals." Metallurgical Reviews 11:159.
7. D. S. Whitmell. 1982. "Immobilization of Krypton in a Metallic Matrix." Nuclear Energy 21:181.
8. H. J. Schmidt, E. Henrich and F. Baumgartner. 1982. "Conditioning and Storage of Fission Product Krypton Using Continuous Ion Implantation into Sputtered Metals." Proceedings of the 16th DOE Nuclear Air Cleaning Conference. CONF-801038, 2:1019, NTIS, Springfield, Virginia.
9. D. S. Whitmell. 1984. "Choice of Materials for the Immobilization of 85-Krypton in a Metallic Matrix by Combined Ion Implantation and Sputtering." 18th DOE Nuclear Airborne Waste Management and Air Cleaning Conference. CONF-840806, 1:667, NTIS, Springfield, Virginia.
10. M. A. Bayne, R. W. Moss and E. D. McClanahan. 1979. "Krypton Entrapment in Continuous Biased Sputter-Deposited Glassy Metals." Thin Solid Films 55:137.
11. R. W. Knoll, and E. D. McClanahan. 1983. "Influence of Composition and Substrate Bias on Structure and Inert Gas Content of Sputter-Deposited Ni-La Alloys." J. Vac. Sci. Technol. A1(2):271.
12. M. A. Bayne, R. W. Moss and E. D. McClanahan. 1978. "Krypton Entrapment in Pulse-Biased Sputter Deposited Metals." Thin Solid Films 54:327.
13. R. W. Knoll. 1985. "A Metastable Phase Diagram for Sputter Deposited Ni-La Alloys." Materials Letters 3:137.

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