POTENTIAL FOR BENEFICIAL USE OF KRYPTON-85

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Large quantities of krypton-85 (about 42 MCi) are contained in stored power-reactor fuels and about 1 MCi/year in fuels processed at each of the Savannah River and Hanford defense fuel-processing plants. This nuclear byproduct could be a significant material resource if used in specialized applications. Recently a technique for implanting krypton in a growing sputter-deposited metallic film has been developed. This yields a stable, high-concentration source of krypton-85 which may have applications for small power generators. Metal deposits containing up to 14 atom% have been prepared that would give a heat source of 0.9 W/cm^3 if fully enriched krypton-85 were implanted. Potential applications for up to 10-W batteries include power for runway lighting and other specialized military applications in remote locations, power for telephone or radio-communications in the far North, and power for monitoring equipment for tracking animals. Krypton-85 has the advantage of being environmentally the most acceptable heat-producing radioisotope available for power production.

KRYPTON-85 PROPERTIES AND AVAILABILITY

Of the many radioactive isotopes generated by the fission of uranium in nuclear reactors, krypton-85 has many unique properties. It is the only rare gas isotope with a sufficient half-life to survive the fuel storage time prior to fuel processing in significant quantities to be a useful radioactive isotope. Thus, this self-heating, nonchemically reacting gas has found utility in several unique applications, particularly in nondestructive examination of materials, in thickness measurements, and in radioluminescent lighting.[1-4]

The krypton-85 content in spent power-reactor fuels is about 8,500 Ci/tonne, with somewhat lesser quantities in defense fuels because of the lower burnup. It is estimated that 42 MCi of Kr-85 could be obtained from existing inventories in power-reactor fuels and about 1 MCi/year from operation of each defense fuel-reprocessing plant at Hanford and Savannah River.[5]

Despite this large volume in stored fuel, krypton-85 is scarce because of the lack of recovery facilities on currently operating reprocessing plants. Several recovery techniques have been considered for fission-product noble gases. Cryogenic separation and selective absorption in fluorocarbon solvents are the leading processes currently under study in the U.S., Europe, and Japan. At present, the only source of krypton-85 in the U.S. is that recovered in a small cryogenic separations plant associated with the fuel reprocessing facility at the Idaho National Engineering Laboratory at Idaho Falls. This source will nearly meet the present demand of about 30,000 Ci/year if operated as scheduled.

Current EPA requirements[6] that limit release of krypton-85 from the nuclear fuel cycle to 50,000 Ci/gigawatt-year of electrical energy from fuel irradiated after January 1, 1983, will make krypton-85 readily available if processing of commercial nuclear fuels is reinstituted. It is certainly true that fission-product krypton is an important national resource potentially useful in a wide variety of applications.

Krypton-85 has a half-life of 10.72 years and decays to stable rubidium-85 by emission of beta rays having a maximum energy of 0.67 MeV accompanied by a low yield (0.41%) of 0.514 MeV gamma rays. The heat produced by krypton-85 decay is 0.623 W/gram, with a specific activity of about 395 Ci/gram.

Fission-product krypton from power-reactor fuel yields about 385 grams/tonne of fuel one year after discharge from the reactor. It is composed of about 6% Kr-85, a few parts per million of the long-lived radioisotope Kr-81, and the remainder a mixture of the stable isotopes Kr-82, Kr-83, Kr-84, and Kr-86. Some applications of krypton-85 can use the fission-product mixture. However, isotope-separation techniques to enrich it as well as remove radioactivity from the stable isotopes would markedly increase the usefulness of both the radioactive and nonradioactive fractions. With the advent of the laser isotope-separation and plasma-separation processes, described earlier in this meeting, more complete and economical enrichment appears possible. In addition, a recently developed process for implanting krypton into a metal matrix for disposal purposes appears to have increased the potential for useful application of the krypton-85.

ION IMPLANTATION PROCESS

Deposition of thin films of metals, and to a lesser extent ceramics, by sputtering is becoming a method of coating frequently used in various applications. In this process, highly energetic gaseous ions are accelerated toward a solid target. Upon impact, they knock atoms from the target, which are deposited on the surrounding surfaces. During deposition, gaseous krypton ions are simultaneously implanted into the deposit, yielding a sputtered-metal deposit containing krypton atoms in concentrations up to about 14 atom%.

Details of the sputtering process have been described earlier.[7-9] The system (represented in

Fig. 1) uses a thermionically supported plasma in which electrons ejected from a heated tungsten filament collide with the low-pressure gas atoms, producing gaseous ions. The ions are then accelerated toward the target, where they sputter atoms from the surface, and also toward the deposit, where they are implanted a few angstroms into the metal surface. Since both sputtering and ion implantation occur at each surface, a net sputtering yield is generated at the deposition surface (substrate) by either pulsing the negative-substrate bias voltage or by continuously maintaining a much smaller negative voltage on the deposit than is placed on the target.

Early in the program, we observed that substrate voltages of about 2500 V (comparable to target voltages) were required to obtain significant krypton concentrations in the deposits of crystalline metals. Therefore, pulsing was required, leading to lower electrical efficiencies. However, with metal alloys which yield an amorphous deposit during sputtering, substrate voltages as low as -150 V gave deposits containing krypton concentrations about twice those obtained for crystalline metals at -2000 to -3000 V. With the amorphous deposits, we achieved not only high krypton concentrations but could also use a continuous-substrate voltage with the inherent higher electrical efficiency. Sputtering parameters and krypton concentrations for several crystalline and amorphous metals and alloys have been reported earlier.[7]

The design of the sputtering chamber depends upon the desired form of the krypton-containing metal matrix. Each chamber, however, must have the following general characteristics:

(1) A plasma chamber able to be evacuated and to maintain a krypton atmosphere of approximately 1 Pa (10^{-5} atmospheres).

(2) A sputtering target composed of metal atoms desired in the deposit, which is water-cooled to remove heat from the bombarding ions. This target must be electrically isolated to accommodate a voltage of -2000 to -3000 V.

(3) A water-cooled substrate surface upon which the krypton-containing metal matrix is deposited. This surface must also be electrically isolated to accommodate a voltage of -200 to -300 V.

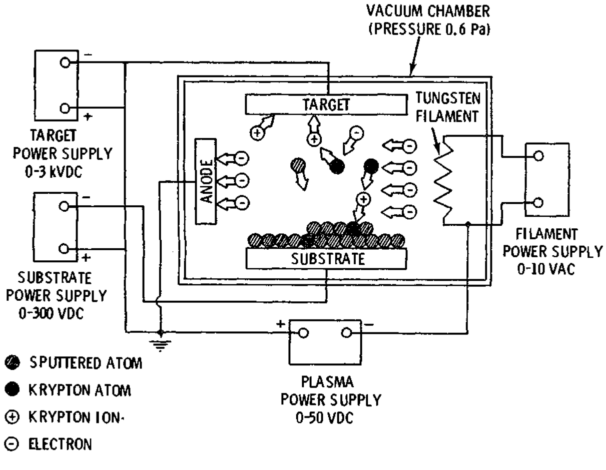

Fig. 1. Thermionically Supported Plasma Sputtering/Ion Implantation System

(4) A source of electrons and an anode to accelerate the electrons and produce krypton ions by collision.

(5) Power supplies with current limiting devices to supply the energy along with necessary control equipment.

The time required for the desired deposit depends upon the sputtering rate of the target, the pressure of the gas, and the current density in the chamber. Experimental systems have been operated in our laboratory which deposit up to about 75 g of the metal alloy/hour with rates up to 150 g/hour easily achievable.

PROPERTIES OF KRYPTON-CONTAINING METAL ALLOYS

The effective use of krypton-85-containing metal alloys will require an understanding of their stability, gas release rates, and other mechanical, thermal, and chemical properties. These properties have been measured on metal alloys containing non-radiactive krypton for a variety of alloys.

The krypton content of several crystalline and amorphous sputter-deposited metal alloys has been reported earlier.[7] The most successful of the alloys in incorporating krypton in their structures and, thus, the most widely studied, have been iron- or nickel-based alloys which contain 10-20 atom% yttrium or lanthanum and up to 14 atom% krypton. If 14 atom% krypton-85 were contained in an alloy with a density of 8 g/cm^3, a continuous heat release would be about 0.9 W/cm^3 at beginning of life, decreasing by a factor of 2 each 10.7 years.

The krypton release rate from the nickel and iron-based alloys is insignificant at temperatures below 300°C but increases with increasing temperature. Depending on the krypton content and the composition, the metal alloys studied thus far release krypton very rapidly at temperatures from 550 to 900°C. It is our belief that refractory metal alloys can be used that will contain the krypton at temperatures above 1000°C.

Most of the krypton-containing alloys studied exhibit excellent resistance against oxidation by air or water. These studies indicate that the alloy forms a thin passive-oxide layer under oxidizing conditions that inhibits further diffusion of oxygen into and krypton out of its surface, thus increasing krypton-retention stability.

Amorphous krypton-containing alloys tend to crystallize at temperatures of 280 to 400°C with negligible loss of krypton. As confirmed by x-ray diffraction studies, the Ni/La/Kr alloy forms hexagonal crystals of Ni_5La at temperatures above 390°C. Other crystallographic transformations, observed by differential scanning calorimetry, occur at higher temperatures.

These krypton-containing, sputter-deposited metals appear to be significantly more brittle than related crystalline alloys but have sufficient strength for most purposes. The coefficient of thermal expansion for a Ni/Y/Kr alloy is 20×10^{-6} °C^{-1} up to 300°C.

A thermal conductivity for the Ni/Y/Kr alloy of 0.06 W/cm-°C at temperatures from 90 to 365°C was observed. This value is markedly reduced from that expected for a nickel-yttrium alloy, probably due to the high content of krypton and the amorphous structure. The properties of sputter-deposited alloys containing krypton are dependent upon several controllable parameters such as composition, deposition temperature, and krypton content. It, therefore, appears that the properties can be tailored, within limits, to match the requirements for various applications.

CHARACTERISTICS OF KRYPTON-85 FUELED POWER SOURCES

The characteristics of the sputter-deposited amorphous metals appear ideal for use in isotope power sources because of the high krypton content and the stability of the deposit. In addition, the use of the chemically inert, gaseous isotope decreases markedly any potential hazard to the environment in the event of its release. Krypton concentrations in excess of one gram/cm^3 have been achieved in our laboratory. This concentration is equivalent to a pressure of 295 atmospheres (4340 psi) at 27°C for an encapsulated gaseous source.

As stated earlier, these solid heat sources have been shown to be stable with very slow krypton release rates up to at least 400°C, and some systems demonstrate stability to 750°C. We believe that even higher temperature stability can be obtained using more refractory metals.

The heat can be converted to power by several techniques. It appears, however, that direct conversion using currently developed thermoelectrics is preferable for most applications because of its simplicity and reliability. Direct thermoelectric conversion does suffer from the low conversion efficiency of 6 to 8%, resulting in a larger size and krypton requirement for the conversion unit. It appears, however, that compared with other isotopic sources these solid krypton-containing alloys may be competitive where only small power sources are required and where a relatively small radiological shield is acceptable. Furthermore, the krypton-containing systems have the advantage of being both biologically and chemically inert and, thus, may be more acceptable environmentally.

A 5-watt battery using 8% efficient thermoelectrics would require a 62.5-watt heat source containing 40,000 Ci of Kr-85. To minimize the size, fully enriched Kr-85 is anticipated. If this krypton were encapsulated into an alloy with a nominal composition of $Ni_{0.81}La_{0.09}Kr_{0.10}$, proposed for a storage medium, a deposit weighing about 770 grams would result. This deposit would have a volume of about 96 cm^3 (a sphere 5.6 cm in diameter). Thus, with a dense metal shield, the entire system would probably be from 10 to 15 cm in diameter. These batteries would have a lifetime of about 10 years, with a decrease in power of 50% during this period. Moreover, their self-heating would prevent the adverse impacts of cold climates.

POTENTIAL APPLICATIONS

Although many possible applications may be envisioned for the metal-krypton alloys, their use as heat sources for small, environmentally acceptable batteries appears most promising. Power capacities of these devices would range up to 10 watts. Physical size of the heat-producing element would not exceed 250 cm^3, but shielding requirements may increase the volume about tenfold or double the diameter. Should the power supply be destroyed, the Kr-85 would be dissipated to the atmosphere with minimal hazard since krypton gas is not retained in biological forms. Some specific uses for this sort of device are discussed in more detail in the following paragraphs.

One potential use of these batteries might be for military and defense use in remote areas, particularly in cold climates. High-quality lithium batteries used to power airfield markers and for other purposes function for a maximum of 6 hours when the temperatures drop to -40°F or below. Lifetimes are short even at 0°F. During the recent winter military exercise in Alaska, costs for batteries for lighting and marking purposes for one runway were estimated at $30,000 to $40,000 because of cold weather failure. The lithium batteries have power outputs in the range of 12 watts and are about 6 inches on a side, which may be larger than the proposed Kr-85 batteries. The long life of the Kr-85 battery, its self-heating characteristics and insensitivity to the cold would be valuable assets where battery failure is common. Because the batteries could be designed to have a nominal lifetime of between 5 to 10 years, they could be stored during summer months, and thus costs would be reduced and reliability increased.

Another use for such a battery would be to power Arctic telephones, radiophones, repeater devices, and civilian communications devices. For example, there are many miles of remote highways in Alaska and northern Canada where telephone or radio communication is unavailable because of lack of power. In winter, breakdown of equipment can be fatal unless a means of communication is available at a reasonable distance or another traveler appears soon. Kr-85 batteries could be used to power telephones and repeater stations along these roadways to reduce the hazard to the Arctic traveler and at specific locations along the ice roadways that are constructed only for winter travel. As in other cold weather applications, these batteries would be unaffected by the cold and provide safe reliable power to keep vital equipment functioning.

Another potential use of these batteries might be to track the movement of animals. Large marine mammals such as whales, porpoises, seals, and fishes such as sharks and rays are being studied to establish their territorial requirements, populations, breeding habits, physiology and other factors affecting their life cycles. These factors are also being studied for large Arctic terrestrial animals such as moose, polar bear, and caribou in efforts to ensure their survival. Ordinary batteries perform badly or not at all in many of the environments encountered in these studies and also have lifetimes of less than 1 to 2 months under the best conditions. Krypton-85-powered batteries of up to 5 watts would increase the useful life available to such monitoring equipment by several years.

CONCLUSION

The use of high-concentration krypton-metal alloys to fuel thermal-to-electrical converters has potential for application to several specialized power requirements. These applications would use large quantities of krypton-85 and, thus may beneficially use all the fission-product krypton-85 generated. Currently, krypton-85 is in very short supply because of limited recovery facilities. Present demands, however, are only a very small fraction of that generated in the nuclear fuels. Thus, if krypton separation were undertaken in fuel-processing facilities, large quantities might be available. In addition, for heat-source application to be feasible, enrichment of the krypton-85 would be required.

In this paper we have described the development of solid-metal matrices containing krypton in higher concentrations than normally considered in any other form and have examined the feasibility of large use of Kr-85 in meaningful applications.

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