Preparation of Ultrapure Thorium Under Outer Space Conditions

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Introduction

ONE of the most effective methods of purifying refractory metals is by electrotransport at high temperatures. In this process, a direct current is passed through a metal rod (sample), thereby heating it resistively and simultaneously producing electrotransport. Purification occurs as the charge carriers transport impurities with them, so that the impurities are swept to one of the ends of the rod, thus purifying a major portion of the rod. The earliest electrotransport work was that of Seith and Kubaschewski[1] in 1935 on the movement of carbon in iron. The potential for applying electrotransport for the ultrapurification of metals has been described by Verhoeven[2] and Peterson.[3] The purity attainable by this technique has been limited by the presence of the residual gases in the Earth's atmosphere even under so-called high vacuum conditions.

Another problem that is often encountered in the electrotransport purification of polycrystalline metals in earth-bound experiments is that of high-temperature "grain sliding," which is a displacement of the grains due to plastic deformation caused by the weight of the sample. This sliding becomes apparent after only one or two days of heating and, as a result, a region of high electrical resistance often develops resulting in localized overheating and premature termination of the experiment.

Both of these limitations to terrestrial electrotransport processing could be overcome in the noncontaminating, microgravity environment of a molecular shield device. A theoretical analysis of the density within a hemispherical molecular shield has been made by Hueser and Brock.[4] From this analyses, Melfi et al.[5] have shown that the atmospheric component (atomic hydrogen) of the gas density within the shield corresponds to an equilibrium pressure of $\sim 3 \times 10^{-14}$ Torr (N_2).

The purpose of the present study was to develop a prototype electrotransport apparatus and test it in a simulated space environment to evaluate if ultrapurification of refractory metals could most effectively be accomplished in an orbiting low-density materials laboratory.

Experimental

In previous work,[6] the authors have reported that the ultrapurification of thorium metal by electrotransport refining is highly sensitive to the background gas density in which the refining takes place. As a result of this study, thorium metal specimens having resistance ratios ($R_{300K}/R_{4.2K}$) of 2000 (once refined) and 4200 (twice refined) were prepared for polycrystalline samples, and resistance ratios of 1700 and 1800 were obtained for single crystals.

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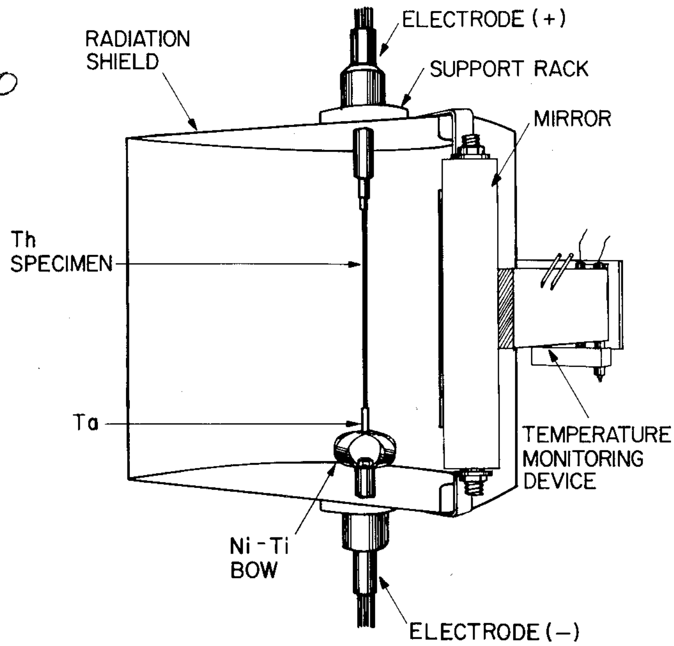

Fig. 1 Schematic of the electrotransport apparatus used to prepare high-purity thorium under simulated space conditions.

In the following subsections, some of the engineering detail and experiments are described that were essential to the successful development of the prototype electrotransport experiment. The electrotransport apparatus developed for this work is shown schematically in Fig. 1. The apparatus was attached to the wall of a hydrocarbon-free space simulation chamber in which a pressure of 3×10^{-12} Torr (N_2) was routinely achieved.

Determination of Sample Size

The ideal length of the sample for a six-day orbit was determined from the electric mobility U and the diffusivity D for the interstitial solutes in thorium at 1500°C. These values, along with the respective values for the electric field E, are shown in Table 1 and were used in Verhoeven's steady-state equation[2] to determine that a sample length of 16.5 cm was most suitable for the experiment. A sample of this length could be electrotransport purified to reduce the nitrogen and oxygen to 2×10^{-15} and 1×10^{-16} of their original concentrations, respectively. Carbon, which migrates considerably slower, would be decreased to less than 1×10^{-3} of its original concentration.

Sample Assembly

The sample assembly consists of a thorium specimen and three adapters that connect the specimen to the electrodes. These adapters include the tantalum cathode adapter, the thorium anode adapter, and the 0.015-cm-thick bow-type adapter fabricated from a Ni-Ti memory alloy.[7] Tantalum was used as the cathode adapter since solutes migrate against the electron flow of electrons in this metal,[8] that is from the anode to cathode, and therefore no impurities from the adapter could migrate into the thorium specimen. Thorium metal was used as the anode adapter since it served as a sink

Table 1 Electrotransport parameters in thorium at 1500°C for a 0.254-cm-diam rod

	E, V/cm	U, 10^{-4} cm^2/V-s	D, 10^{-5} cm^2/s
Carbon	0.154	1.4	1.9
Nitrogen	0.151	8.0	2.9
Oxygen	0.156	16.0	5.5

for the solute impurities electrotransported from the thorium specimen. Before the Ni-Ti bow was used in an experiment, it was preset by mounting in a holder and deflecting it the 0.26 cm necessary to compensate for the thermal expansion of the rod. The memory was then set by heating in vacuum to 480°C. The bow was removed from the holder, expanded, and connected to the tantalum adapter. In this manner, as the thorium rod was resistively heated and the bow reached ~45°C, the bow assumed its memory shape, which allowed the thorium rod to expand into a relaxed condition. The thorium rod was thereby kept straight during heating and was contained with a minimum amount of force.

Sample Heating System and Temperature Monitoring Device

The automatic electronic equipment used to resistance heat the thorium rod to a desired temperature, consisted of a power supply, programmer, and a data acquisition system. The programmer consisted of an electromechanical processor and used an analog to digital (A/D) converter and a digital to analog (D/A) converter. In this system, the A/D converter was triggered to sample the voltage after the sample was heated to 1600°C with a direct current of 86.5 A. The output of the converter was used by the D/A converter to drive the programmed power supply to furnish the voltage. In this manner the voltage was controlled during the six-day electrotransport experiment and an increase in the resistance of the sample assembly would result in a power decrease and, consequently, a slight cooling of the sample.

The temperature monitoring device (TMD) is shown schematically in Fig. 1 and was used to continually observe the heated sample and yet be out of its optical path. This was accomplished by mounting the TMD on the support rack so that it would be directed to a metal mirror which reflected the sample image. The TMD was designed to withstand the six-day, 380°C vacuum bakeout of the space chamber required to minimize the residual gases present.

The details of the sample heating system and the TMD may be found in previous reports.[9-11]

Simulation of Orbital Environment

In separate experiments, thorium rods were purified by electrotransport processing under simulated conditions of coldness and darkness of space and of solar radiation. These experiments were performed in the space simulation chamber under a pressure of 5×10^{-12} Torr (N_2).

Coldness and Darkness: The coldness and darkness of space was simulated by placing a cryogenic panel directly opposite the sample assembly shown in Fig. 1. The panel was fabricated from 304 stainless plate. The front of the panel contained a 0.80 cm thick layer of stainless steel honeycomb which had hexagonal cells measuring 0.08 cm across. This panel, which had an effective surface area of 100 m^2, was kept full of liquid nitrogen throughout the six-day purification experiment and its chilled honeycomb surface had a measured emissivity of 0.90. The electrotransport experiment under these simulated conditions required no increase in power to heat the sample. Substantial decreases in the system pressure in the vicinity of the sample were observed due to the heat absorption capability and cryogenic pumping of the panel.

Solar Radiation: Solar radiation was simulated using a carbon arc lamp which was positioned so that a 15.25-cm-diam beam of collimated light, having a unit solar intensity, was projected onto the thorium sample and the radiation shield for 30 min. A Fresnel lens, placed over the 15.25-cm-diam sight glass of the space chamber, was used to produce a 30-cm-diam circular area of radiation and an intensity of one solar constant. The simulation of one solar constant during electrotransport processing resulted in an increase of sample temperature of only 14°C. During this solar radiation the radiation shield was 45°C hotter than when no radiation was used. This increased temperature resulted in the residual gas pressure in the vicinity of the sample reaching 3.0×10^{-10} Torr, which should present no problem in the molecular shield device due to its high pumping capacity and its good heat rejection capability.

Conclusion

A prototype electrotransport experiment was developed for the ultrapurification of refractory metals. The apparatus consists of a sample assembly, radiation shield, and temperature monitoring device. It was designed to withstand heating in vacuum at 380°C for six days to remove surface gases prior to its use in electrotransport refining experiments. Laboratory electronics for the experiment were developed and a totally automatic control system was used to heat the specimens. Electrotransport purification experiments were made under simulated space conditions of coldness and darkness and solar radiation without any adverse effects. It is concluded from this work and from our previous study,[6] that the ultrapurification of small amounts of metals could be most effectively accomplished by electrotransport refining in an orbiting, low-density materials laboratory such as a molecular shield device.

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