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SOLID STATE ELECTRODIFFUSION IN BISMUTH

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SOLID STATE ELECTRODIFFUSION IN BISMUTH

By

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INTRODUCTION

Production of Po^{210} in quantity requires bismuth recovery for recycle. Irradiated bismuth must be processed without delay following reactor discharge, because the short half-life of Po^{210} results in a loss of about 0.5 %/day. A process which quickly recovers the Po^{210} in a volume of material amenable to laboratory scale processing would be ideal.

In studies of electrodiffusion in cerium it was shown that iron and cobalt rapidly concentrated in a small portion of the cerium specimen at the anode end, or were even removed from the specimen by injection into the anode surface.⁽¹⁾ Should this be possible with Po^{210} in bismuth, the process would be of considerable interest. Moreover, processes for recovery of Po^{210} must retain the bismuth in its original state with respect to impurities. The electrodiffusion behavior of various impurity elements in bismuth is therefore of general interest.

The electrodiffusion rate of iron and cobalt in cerium is a linear function of current density and time of current flow. This dependency is typical of most metals studied to date.⁽²⁾ Unfortunately, bismuth is a very poor electrical conductor, and the current density that can be attained without destruction of the specimen by melting is severely limited. This disadvantageous situation can be partially overcome by the technique of cooling the specimen during passage of the electric current.⁽³⁾ The results of measurements utilizing this technique are reported here.

SUMMARY

- (1) A 5 in. long by 3/8 in. diam bismuth bar clamped between 3/4 in. diam aluminum electrodes will melt near its center upon passage of a current slightly in excess of 85 A/cm^2 .
- (2) When a specimen is immersed in a nonvolatile hydrocarbon oil circulated over cooling coils situated near the specimen, successful electrodiffusion runs of up to 330 hr were achieved at current densities of 260 A/cm^2 . This represents a power density increase of about an order of magnitude.

- (3) Despite attainment of practical current densities over prolonged periods, no electrodiffusion of Po^{210} , of a tellurium "stand-in," or of trace impurities in bismuth was observed.
- (4) Heated by a dc current, the specimens exhibited a temperature gradient of from 120 to 140 C from the center to the ends. This thermal gradient produced slight diffusion (Soret effect) of Po^{210} from the hot center toward the cold ends. Diffusion rates were, therefore, not limiting. Po^{210} was simply not affected by the passage of the electric current. This implies that the effective valence of bismuth and of Po^{210} is the same and the electric field will not accelerate Po^{210} with respect to the bismuth lattice. Additionally, the cross-section for electron momentum transfer effects must be quite similar for both bismuth and Po^{210} , or extremely small.

EXPERIMENTAL

Due to the hazard of experimental work with Po^{210} , tellurium was employed as a stand-in in preliminary work of equipment development and testing. Bi-Te alloys of nominally 0.5 and 0.05 wt% Te were prepared by melting these metals together in a graphite crucible heated with an insulated resistance winding. After thorough stirring with a graphite rod, the melt was poured into 3/8 in. diam by 7 in. deep holes in a split graphite mold dressed with ZrO_2 . The easily portable electrically heated pouring crucible and split graphite mold were later transferred to a gloved hood and used for preparing specimens traced with Po^{210} .

The electrodiffusion cell consisted of a 10 in. desiccator covered with a brass plate sealed to the desiccator with a neoprene O-ring. Two 3/4 in. diam aluminum electrodes projected into the desiccator and were insulated from the brass plate by Teflon[®] inserts. Each electrode was hinged in two places so the specimen connected to them could expand and contract without stress. The ends of the electrodes were slotted to receive the 3/8 in. diam bismuth alloy specimen. The specimen was held securely by set screw pressure bearing against a sliding aluminum piece inserted in the slot after the specimen was

in place. These small aluminum pieces contained thermocouples that sensed the temperature at the electrode ends of the bar and also detected high resistance contacts.

When operating with oil coolant, the desiccator was filled with 1 gal of vacuum pump oil. Two 1/4 in. diam cooling coils carrying cold water entered through the brass plate. One cooling coil was a simple loop in a plane 1 in. above the plane of the specimen. The other was a double loop in a plane 1 in. below the plane of the specimen.

The oil was circulated with a magnetic stirrer, but this proved unsatisfactory. A line carrying argon to blanket the oil was lowered to the bottom of the desiccator so the argon bubbles would provide additional agitation. With this arrangement, the oil temperature 1/4 in. from the surface of the specimen did not exceed 45 C with the specimen surface at 240 C.

The surface temperature of the specimen midway between the electrodes was sensed by a Chromel-Alumel thermocouple taped to the specimen with fiberglass tape and then clamped tightly with a brass hose clamp. The signal from this thermocouple was fed to a precision temperature control unit. This unit controlled a saturable reactor feeding power to a bank of selenium rectifiers that supplied dc power to the specimen.

Due to slight variations in cooling efficiency resulting from random oscillations of the magnetic stirring bar, current fluctuations of ± 5 A were noted. The surface temperature of the bar remained constant to within about 1 to 2 C° during these fluctuations.

RESULTS AND DISCUSSION

Preliminary runs were made to determine the failure point of specimens in argon and in oil and to determine the electrodiffusion rate of tellurium and of minor impurities at two different current densities. The work was concluded with a single run on a Po^{210} traced specimen.

In argon a 3/8 in. diam by 5 in. long Bi-0.05 wt% Te alloy will attain a surface temperature of 250 C at a current density of 85 A/cm². From the equation:⁽⁴⁾

$$T_c - T_s = \frac{E i R^2}{4 J k} \quad (1)$$

where

T_c = temperature at specimen center

T_s = temperature at specimen surface

E = potential drop, Joules/coulomb/°

i = current density, coulombs/cm²/sec

$R_2 = 0.2268 \text{ cm}^2$

$J = 4.185 \text{ Joules/cal}$

k = heat transfer coefficient, cal/cm-sec/°,

it can be calculated that the temperature at the center of the specimen is 260 C. This condition can be maintained as a steady state, but a slight increase in current density results in specimen melting.

With a circulated oil coolant, a similar specimen failed at a current density of 310 A/cm². The oil quenched the arc quietly with no oil ejection or fire hazard. Had Po²¹⁰ been present, it appears probable that it would have been satisfactorily contained by the oil. The oil coolant permits sustained operation at a power density at least an order of magnitude greater than can be attained in argon.

Two runs were made using a 0.5 wt% Te-Bi alloy (Runs 1 and 2) and one run was made using bismuth traced with Po²¹⁰. The conditions prevalent during these runs are outlined in Table I.

In these experiments the voltage drop measured across the electrodes and specimen ranged from 1.4 to 2.0 V but varied somewhat erratically during a run and from run to run as a result of variable resistance in the sliding contact at hinges in the electrodes. For calculations of the core temperature, a 1.0 V potential drop through the specimen was assumed in all cases.

TABLE I
EXPERIMENTAL CONDITIONS DURING ELECTRODIFFUSION
OF Bi-Te AND Bi-Po²¹⁰ ALLOYS

Run	Surface Temperature, C (Center)	Core Temperature, C (Center)	Anode End Temperature, C	Cathode End Temperature, C	Current Density, A/cm ²	Run Duration, hr
1	170	180	115	105	197	230
2	225	239	104	100	250	240
3(a)	240	255	115	105	270	330

(a) Specimen traced with Po²¹⁰.

At the conclusion of a run, the specimen was sawed into segments approximately 1.0 cm long. The tellurium content of these was determined by comparing the ratio of the intensities of the X-ray fluorescence tellurium $k \alpha_1$ line and bismuth $L V_1$ line. While this procedure does not yield an absolute determination of the tellurium concentration, it does yield an accurate measure of changes in concentration. No change in tellurium concentration occurred under the conditions of Runs 1 and 2.

The results of emission spectrographic analysis of segments of the specimen from Run 2 are shown in Table II. These are semiquantitative

TABLE II
SPECTROGRAPHIC ANALYSIS OF SEGMENTS CUT
FROM SPECIMEN USED IN RUN 2

	Concentration (wt%) in Segment at the Following cm from Cathode End										
	1	2.2	3.3	4.8	5.5	6.8	8.1	9.2	10.6	11.7	12.7
Silver	0.05	0.05	0.03	0.03	0.02	0.02	0.02	0.02	0.02	0.02	0.07
Copper	0.005	0.003	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002
Iron	0.005	0.005	0.001	0.0005	0.0005	<0.0005	0.0005	0.005	0.001	0.007	0.005
Magnesium	0.0005	0.0005	0.0001	0.0001	<0.0001	<0.0001	0.0001	0.0001	0.0005	0.0005	0.0007
Lead	0.005	0.005	0.005	0.005	0.005	0.005	0.005	0.005	0.005	0.005	0.005
Silicon	0.0005	0.001	<0.0001	0.007	<0.0001	<0.0001	0.0001	0.0001	0.0001	0.0005	0.0005

results. Values shown are the concentrations (in wt%) at the given distance from the cathode end. No other impurities were detectable. Like tellurium, lead shows no concentration change over the length of the specimen. The remaining trace impurities diffuse away from the center of the bar, but there appears to be no accumulation at one end and decrease at the other end which would be indicative of an effect due to the electric current. It appears that the effect observed is due to the thermal gradient (Soret Effect).

A similar result was observed when segments from Run 3 were analyzed for Po^{210} . These segments were weighed and counted in a gamma-scintillation counter. The results shown in Table III are expressed as counts/min/g. As shown by these data, Po^{210} diffuses away from the center, but does not concentrate at one end in preference to the other. As above, this behavior must be attributed to the effect of a thermal gradient.

TABLE III
EFFECT OF A THERMAL GRADIENT ON Po^{210}

Distance from Cathode, cm	Po^{210} Concentration, counts/min/g
1.2	76.8
2.5	70.3
3.4	64.8
4.8	61.2
6.0	56.5
7.3	59.0
8.9	52.7
10.2	53.6
11.5	67.1
12.7	81.2
Original Material	88.8 ^(a)

(a) This sample had somewhat better geometry for counting. This result is therefore slightly high.

The evidence showing that thermal diffusion occurs indicates that the inherent diffusivity of these elements is sufficiently large that electrodiffusion should have been observed within the time intervals studied. That electrodiffusion was not observed must, therefore, be attributed to a lack of interaction between the solutes of interest and the electric current. Two kinds of interaction are normally observed. These are momentum transfer effects and potential field effects.

At normal temperatures bismuth exhibits the largest positive Hall coefficient of any element ⁽⁵⁾ If the Hall coefficient remains positive at the temperatures employed here, then conduction is primarily via defect electrons. Anode directed momentum transfer from electrons will, therefore, be at a minimum, and it is difficult to visualize occurrence of cathode

directed momentum transfer from defect electrons (holes). Such an effect has been postulated, however, to account for the behavior of iron. (3)

The potential field effect requires that solute atoms ionize to yield species with a net charge different from that of the charge on solvent metal ions. In the absence of an appreciable charge difference there will be no net movement of solute atoms relative to the solvent lattice. The results obtained imply that the solute atoms in bismuth do not acquire a charge appreciably different from that on bismuth. The system may, in fact, be neutral.

CONCLUSION

By accelerating the rate of contact of fresh coolant with the specimen surface and by changing to a coolant with a larger heat transfer coefficient, it should be possible to increase the current density applied to the bismuth specimens by a factor of two or three. Such a "tour de force" does not seem warranted in view of these results, for to be of practical significance Po^{210} must be caused to concentrate at one end of the specimen rapidly. Even at such high current densities, it does not appear that run times could be shortened significantly; and in 240 hr, for instance, the loss of Po^{210} by radioactive decay has reached the level of 5%. It must therefore be concluded that the process of electrodiffusion is useless for Po^{210} concentration and of little or no value as a purification technique when applied to bismuth.

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