JOURNAL OF MATERIALS SCIENCE 27 (1992) 4223–4229

Intercalation of copper into bismuth telluride

J. B. MACLACHLAN, W. H. KRUESI*, D. J. FRAY**
Pilkington Technology Centre, Hall Lane, Lathom, Ormskirk, Lancashire, UK
**CATO Research Corporation, 5040 Tabor Street, Wheatbridge, CO 80033, USA*
***Department of Mining and Mineral Engineering, University of Leeds, Leeds LS2 9JT, UK*

The intercalation and leaching of copper into and out of bismuth telluride was investigated using aqueous and solid state electrochemical methods. It was found that copper intercalates up to a concentration of 3 mg/g bismuth telluride. Copper may also react with bismuth telluride to form copper telluride (Cu_2Te). Boiling hydrochloric acid leaches, or controlled potential electrochemical leaches, were effective at removing intercalated copper from bismuth telluride, returning the bismuth telluride to its original, undoped state. E.m.f. measurements using a solid, copper-ion conducting electrolyte resulted in copper activities of between 0.000 73 and 0.044 for intercalated bismuth telluride. An effective copper diffusion coefficient of 4×10^{-5} cm^2 s^{-1} was measured for a sintered polycrystalline bismuth telluride pellet at 483 K.

1. Introduction

The thermoelectric properties of bismuth telluride were first discovered in 1954 [1]. Bismuth telluride is still regarded as the best simple compound for use in thermoelectric refrigeration; and for this purpose it is surpassed only by solid solutions in which it is the major component.

Microscopic and qualitative X-ray investigations have indicated [2] the existence of only one compound, Bi_2Te_3, with a broad range of homogeneity. The crystal structure of Bi_2Te_3 is rhombohedral with the space group D_{3d} (R3m) [3] and it is isotypic with Bi_2Te_2S and Bi_2Se_3. Bismuth telluride crystals are made up of layers of like atoms stacked in the rhombohedral $\langle 1\,1\,1 \rangle$ direction (parallel to the *c*-axis), with the sequence

$$-Te^{(1)}-Bi-Te^{(2)}-Bi-Te^{(1)}-Te^{(1)}-Bi-Te^{(2)}-Bi-Te^{(1)}-$$

The neighbouring $Te^{(1)}$ layers are held together by very weak Van der Waals forces, whereas it is thought that bonds between bismuth and tellurium atoms are predominantly covalent. Consequently, bismuth telluride crystals can be cleaved readily along planes perpendicular to the *c*-axis and bismuth telluride shows a marked anisotropy in many of its properties.

Bismuth telluride can be produced with either p- or n-type conduction by controlled deviations from exact stoichiometry [4]. An excess of bismuth gives p-type properties, perhaps because some bismuth atoms occupy tellurium sites, and an excess of tellurium gives n-type properties. Also, lead as an impurity gives a p-type material, and copper, silver, bromine and iodine give n-type conductivity.

The layered structure of bismuth telluride leads to the strongly anisotropic diffusion of certain impurities in the material, the most striking effect being observed with copper. This has been noted [5] in the manufacture of thermoelectric devices when p-type bismuth telluride is soldered to a metal conductor. The use of a copper bit on the soldering iron leads to the conversion of the whole block (typical size – 3 mm × 3 mm × 6 mm) to a highly doped n-type material in the few seconds required for soldering. This means that both the solder and soldering bit have to be copper free if conversion of the p-type material is to be avoided. The rapid diffusion of copper may also lead to problems if copper is deliberately added as a dopant to produce n-type material, as on standing, even at room temperature, copper may diffuse to the surface of the bismuth telluride where it can oxidize, and the copper may also form internal precipitates, thus making the material become less n-type.

The diffusion coefficients of copper along the *a*- and *c*-axes of bismuth telluride have been measured [6] using a radioactive isotope of copper. Samples of bismuth telluride were cut from polycrystals consisting of a few crystallites oriented along the growth axis with exposed faces either parallel or perpendicular to the cleavage planes. Copper was electroplated on to the surface and the rate of diffusion measured under an atmosphere of hydrogen using a scintillation counter to determine the copper concentration of grindings of the material. It was found that, at room temperature, the two diffusion coefficients differed by about nine orders of magnitude with fast diffusion along the cleavage planes. In order to account for the rapid diffusion, it is thought that the copper, between the tellurium layers, can move through a region of relatively weak electrostatic bonding forces and large layer spacings. In any other direction covalent and ionic bonding between tellurium and bismuth atoms would make penetration more difficult. Similarly, the

This work was conducted at the Department of Materials Science and Metallurgy, University of Cambridge, Cambridge CB2 3Q2, UK

0022–2461 © *1992 Chapman & Hall*

diffusion of silver and gold in the parallel direction is relatively rapid, though not quite so fast as that of copper.

The intercalation of copper into bismuth is obviously a problem in the soldering of bismuth telluride, but there may be circumstances where the effect could be used to advantage. For instance, in the manufacture of circuit boards holding many microelectronic devices, soldering of copper or copper-containing connection wires is performed by dipping the protruding wire ends on the circuit board into a bath of tin solder to coat the wire ends with solder. However, the tin bath picks up copper from the wires, and when the copper concentration in the solder reaches a high enough level the solder ceases to wet the wires. If the copper could be intercalated into a layered compound, this may offer an easy way of removing the copper, especially as Goodman [5] has reported that the copper can easily be removed by treating the intercalated bismuth telluride with concentrated acid. Similar approaches, using different materials, have been reported by Celik and Fray [7] and Hardeman and Fray [8]. As there is only brief mention of the intercalation of copper into bismuth telluride in the literature, this work was undertaken to investigate the amount of copper that can be intercalated into bismuth telluride.

2. Experimental procedure

2.1. Materials – methods of preparation

Two sources of bismuth telluride were used. The purchased high-purity polycrystalline bismuth telluride had the following impurity levels [9] (p.p.m.): copper 1; iron 1; lead < 1; magnesium < 1; silicon < 1; silver < 1. The high-purity bismuth telluride was a very porous, powdery material in the form of irregularly shaped and sized lumps, and had a rather low mechanical strength. In order to obtain samples of a suitable size and strength, the material was crushed to uniform small crystals which were packed into a stoppered rubber tube (0.85 cm diameter, 3.3 cm length). The crushed powder then underwent cold isostatic pressing, with a peak load of 400 kN, giving a peak pressure of approximately 6.3×10^9 Pa. On removal from the tube the pressed material fell into small pellets with a 0.65 cm diameter and up to 0.4 cm length. These were then sintered in a sealed quartz tube under vacuum (3×10^{-3} Pa), for 4 h at 725–741 K. The apparent density of the sintered pellets was 7.5 g cm^{-3} which is 97% theoretical density.

Polycrystalline bismuth telluride was also prepared from the direct reaction of pure bismuth and tellurium. A mixture of 48 wt % Te, and 52 wt % Bi was melted under vacuum in a sealed quartz tube at 923 K for 6 h. The resulting bismuth telluride was used to prepare directionally solidified bismuth telluride. Small lumps and powder were placed in a sealed quartz tube under vacuum. The tube base was initially placed 20 cm from the top of a furnace so that the bismuth telluride granules were in the hot zone of the furnace. The furnace temperature was held at 873 K for 30 min to melt the material. The tube was then lowered 1 cm every 20 min in order to directionally solidify the melt, starting in the curved tube base. The resulting cylindrical pellet was cut with a diamond saw into two pieces.

X-ray powder diffractometry was performed on the bismuth, tellurium, vacuum-melted bismuth telluride and the high-purity bismuth telluride in order to confirm the composition of the materials.

2.2. Measurement of conductivity type of bismuth telluride

The conductivity type of the various bismuth telluride samples was determined by measuring a thermal e.m.f. across the sample. A hot probe touching an n-type semiconductor becomes positive with respect to an ambient temperature contact placed on the same material. For a p-type material the polarity of the contacts is reversed. A small soldering iron was used as the hot probe, and a digital millivoltmeter was used to measure the potential difference between the probes. It was noticed that the exact magnitude of the potential difference seemed to be dependent on the relative positions of the two probes on the bismuth telluride; however, the sign of the potential difference remained fixed. Furthermore, the absolute value of the potential difference appeared to increase with the temperature of the hot probe.

2.3. Electroplating of copper on to bismuth telluride

Electrodeposition was chosen as a suitable method of plating copper on to bismuth telluride pellets; and was followed by annealing to enhance the intercalation of the copper into the material. The bismuth telluride samples, which were cut so as to expose a face with the maximum cross-sectional area perpendicular to the cleavage planes of the bismuth telluride, were wrapped in a coil of nickel wire to act as an electrical contact. All other faces of the sample were coated with a waterproof silicone rubber compound so that only the desired face was exposed, and to prevent preferential electroplating of the nickel wire by copper. The arrangement, using copper nitrate solution as the electrolyte and pure copper as the anode, is shown in Fig. 1. The charge passed was measured using either a coulometer or an ammeter and stopclock, and was used to calculate the amount of copper transferred to the bismuth telluride.

In order to obtain a fairly compact and well adhering copper layer on the substrate, it was necessary to use a low current density of ~ 0.05 A cm^{-2}. At higher current densities the copper deposit was porous and easily knocked or washed off, and at still higher current densities (~ 0.5 A cm^{-2}) a gelatinous blue precipitate was formed. This was probably due to a depletion of copper ions near the cathode as a result of the high current densities, and the resulting polarization of the electrode forced a subsidiary reaction such as the breakdown of the nitrate ion. The silicone rubber provided an adequate barrier to copper deposition on all but the exposed faces. Once sufficient

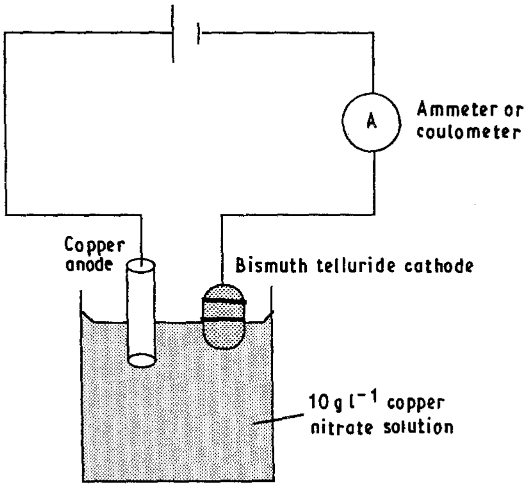

Figure 1 Cell for electroplating copper on to bismuth telluride.

copper had been deposited on the samples to give a fairly uniform coating, the samples were washed and allowed to dry. The silicone rubber was then removed prior to annealing of the specimens, because the annealing temperature was well above the melting point of the rubber. This created some problems as the bismuth telluride tended to flake off with the rubber, and also some copper, which had plated close to the rubber edge, was removed making it difficult to estimate how much copper was available for intercalation.

Samples were annealed at 623 or 673 K for about 4 h in an atmosphere of 5%–20% hydrogen in inert gas (gas flow rate 1–2 cm^3 s^{-1}). The hydrogen–inert gas mixture was used to prevent oxidation of the copper to copper oxide at the copper–bismuth telluride interface. Samples were removed from the furnace after cooling to room temperature, and then weighed and examined.

2.4. Leaching of copper from bismuth telluride

Two methods of removing intercalated copper from the bismuth telluride were used. The first was the boiling hydrochloric acid leach mentioned by Goodman [5]. Pellets were boiled in a test tube containing concentrated hydrochloric acid ($\sim$ 12 M) for up to 4 min. The HCl was then decanted from the test tube, and diluted to 10 cm^3 with distilled water. Various dilutions of this solution were then analysed using atomic absorption spectroscopy against prepared standards to determine the concentrations of bismuth and copper present in the leach.

The second method used was an electrochemical leach which was in essence a reversal of the electrochemical cell used to deposit copper on to the bismuth telluride. A schematic diagram of the electrochemical stripping cell is shown in Fig. 2. A salt bridge and two baths of electrolyte were used to prevent deposition of leached copper on to the silver cathode thus, allowing the amount of copper in the electrolyte to be determined. The potential difference between the bismuth telluride anode and a saturated calomel electrode was monitored on a chart recorder. Conditions of constant current were used in order to be able to estimate the amount of charge passed through the cell and so to obtain a current efficiency for this process. The electrolyte from the bath into which the bismuth telluride had been placed was analysed by atomic absorption spectroscopy for copper and bismuth.

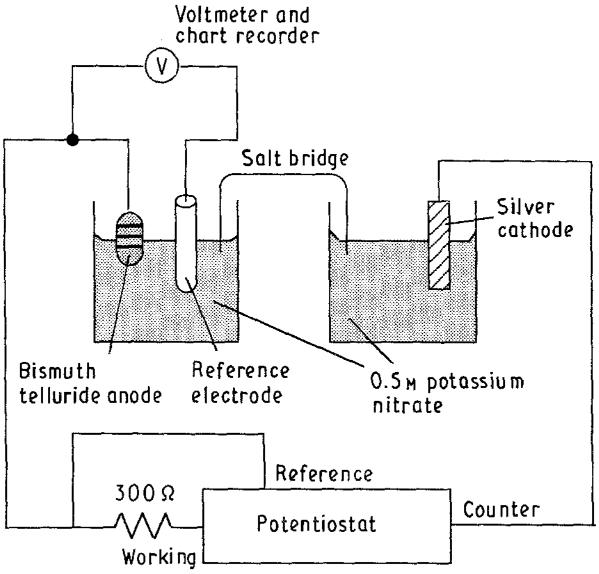

Figure 2 Electrochemical leaching of copper.

2.5. Dissolution of pellets

In order to determine whether all the copper had been leached from the samples by these methods, selected samples were completely dissolved in concentrated nitric acid and the resulting solutions were analysed by atomic absorption spectroscopy.

As toxic hydrogen telluride gas could be produced during dissolution via the reaction

$$Bi_2Te_3 + 6HNO_3 \rightarrow Bi(NO_3) + 3H_2Te \quad (1)$$

the dissolution was done in a stoppered flask with gas entrance and exit ports. The gases exiting the flask were passed into a solution of lead acetate where the precipitation of lead telluride by the reaction

$$H_2Te + Pb(CH_3COO)_2 \rightarrow PbTe(s) + 2(CH_3COOH) \quad (2)$$

prevented the release of hydrogen telluride.

2.6. Activity measurements

One way to determine how strongly the copper is held in the bismuth telluride lattice is to measure the activity. This can be achieved by interfacing the bismuth telluride with a copper-ion conducting solid electrolyte, such as $Rb_4Cu_{16}I_7Cl_{13}$, and measuring the potential across the electrolyte when copper is interfaced with the other side. The cell can be represented by

$$\text{Pt, Cu } (Bi_2Te_3) | Rb_4Cu_{16}I_7Cl_{13} | \text{Cu, Pt}$$

The potential generated across the electrolyte is given by the Nernst equation

$$E = -\frac{RT}{ZF} \ln \frac{a_{Cu'}}{a_{Cu''}} \quad (3)$$

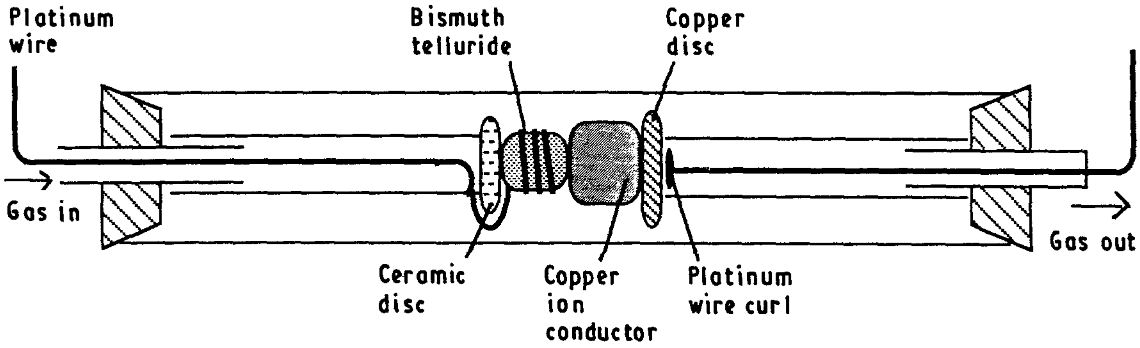

Figure 3 Electrochemical cell in furnace tube.

where Z is the charge carried, E is the potential measured with a high impedance voltmeter, F is Faraday's constant, R is the gas constant, T is the temperature, $a_{Cu'}$ is the activity of copper in the bismuth telluride, and $a_{Cu''}$ is the activity of pure copper, which is taken as unity.

A schematic diagram of the experimental cell is shown in Fig. 3. Nitrogen was passed over the cell to prevent oxidation. Copper was plated on to the bismuth telluride by transferring copper ions across the electrolyte by making the copper the anode and the bismuth telluride the cathode. The voltage across cells in the temperature range of 423–483 K was monitored using a Keithley 610 C electrometer and the values stored using a chart recorder. Using this technique, it was possible to determine both the capacity of bismuth telluride for copper and the activity of the intercalated copper.

3. Results

3.1. Preparation of materials

3.1.1. Vacuum-melted material

The material produced by vacuum melting stoichiometric quantities of pure bismuth and tellurium consisted of large crystallites which were prone to flaking along cleavage planes. The material was quite soft, comparable with elemental tellurium. The conductivity type of the vacuum-melted material was found to be p-type, possibly due to an excess of bismuth, whereas the purchased high-purity material, was found to be n-type, possibly due to an excess of tellurium. The X-ray diffraction traces of the vacuum-melted material and the high-purity bismuth telluride were identical. Thus, it was concluded that for the purpose of these experiments vacuum melting represents a suitable way of preparing bismuth telluride.

3.1.2. Sintered pellets

The pellets produced by the cold isostatic pressing and sintering of high-purity bismuth telluride were mechanically far more robust than either the porous high-purity material or the vacuum-melted bismuth telluride. These pellets were particularly suitable for use in the electrochemical cell with a solid electrolyte owing to their regular shape. Their conductivity was n-type, consistent with the results of George *et al.* [10].

3.1.3. Directionally solidified pellets

On removal of the quartz tube from the vertical furnace it was found that most of the bismuth telluride had collected at the base of the tube on melting. On solidification it had formed a pellet which appeared to consist of only a few large grains. Some bismuth telluride was left adhering to the sides of the tube, as it wets and, perhaps, reacts slightly with quartz. After cutting, the directionally solidified pellets, which weighed about 1 g each, exhibited p-type conductivity.

3.2. Intercalation and leaching of copper

3.2.1. Vacuum-melted bismuth telluride

22.8 mg Cu was plated from copper nitrate solution on to a 0.7878 g pellet of the p-type, vacuum-melted bismuth telluride. After heat treatment for 3 h 40 min at 623 K in an inert gas-hydrogen mixture, a black powder was seen on the exposed face of the bismuth telluride. The powder was scraped off and, together with scrapings from subsequent annealed copper-plated pellets, was analysed by X-ray diffraction and found to be copper telluride (primarily Cu_2Te). However, not all the copper had formed copper telluride as the conductivity type of the bulk of the material was now found to be n-type, indicating copper doping.

Upon leaching in boiling concentrated hydrochloric acid for 4 min, it was noticed that the acid acquired a pale yellow–green coloration, rather than the blue reported by Goodman [5]. Small pieces of a black precipitate also collected at the bottom of the test tube during vigorous boiling of the specimen. The acid was decanted from the porous black precipitate which was then dissolved in nitric acid and analysed by atomic absorption spectroscopy. The precipitate was found to be mostly bismuth. The conductivity type of the pellet had returned to p-type after leaching.

The plating, annealing, and leaching procedure was repeated on the sample and it was noted that the black precipitate was not observed on the second acid leach. Analysis of the leach solution showed that far more bismuth was removed from the pellet during the first leach than the second. This may be due to the formation of a protective layer on the surface of the material during the first leach, or more probably because the first leach removed most of the excess bismuth in the specimen.

Finally, the pellet was completely dissolved in concentrated nitric acid at room temperature and analysed. Although sufficient copper was leached from the bismuth telluride by hydrochloric acid to switch the conductivity type back to p-type, the final analysis showed that significant amounts of copper remain in the bismuth telluride. However, as this copper does not affect the type of conductivity given by the material, it is likely that the copper has formed a compound such as copper telluride.

A 2.1511 g pellet of vacuum-melted bismuth telluride was electroplated with copper and annealed. Again, a black powder of copper telluride formed on the exposed surface of the sample. Instead of leaching in acid, electrochemical extraction of the copper was used. An initial current density of $1.5\,\mathrm{mA\,cm^{-2}}$ was applied. The potential versus time curve showed that the potential difference between the bismuth telluride anode and a standard calomel reference electrode had a discontinuity at a polarization of 380 mV, and finally became steady at a polarization of 575 mV. The current density was later increased to $8.3\,\mathrm{mA\,cm^{-2}}$, and the steady state polarization then increased to 655 mV. A total charge of 5.22 mA h was passed.

The discontinuity at 380 mV indicates an anodic reaction at a lower potential than the steady state potential at which the experiment was run, possibly due to the dissolution of copper. At higher potential the reaction is most likely mixed, including both the dissolution of copper and of bismuth telluride. This was confirmed by the analysis of the electrolyte which showed the presence of both copper and bismuth. By carefully monitoring and controlling the potential it should be possible to limit the reaction to just the dissolution of the copper. Treatment of the pellet in boiling concentrated hydrochloric acid, following the electrochemical leach, showed that not all of the copper could be removed electrochemically.

3.2.2. Sintered high-purity bismuth telluride

A sintered pellet of the high-purity bismuth telluride was copper plated, annealed, leached, and then completely dissolved. It was found that most of the original deposited copper was accounted for after dissolution of this pellet, although only 2.7% of the copper present in the material was removed by acid leaching. This may be because a very large proportion of the copper was present as copper telluride, or because the hydrochloric acid leach is not as efficient as previously indicated [5].

The procedure was repeated on a similar pellet except that the copper was electrochemically leached at an applied current density of $1.0\,\mathrm{mA\,cm^{-2}}$ with a total charge of 0.38 mA h being passed. Again, the resulting potential trace showed a discontinuity during the approach to a steady state potential. A plateau polarization of 460 mV was maintained for approximately 5 min before the polarization increased to a value of 710 mV which was maintained for the rest of the leaching process. It seems likely that the polarization plateaux correspond to the same processes as those occurring at polarizations of 655 and 380 mV for the vacuum-melted specimen, the difference in the absolute value of the voltages being due to differences in the bismuth telluride used.

3.2.3. Directionally frozen pellet

A p-type piece of directionally frozen bismuth telluride was repeatedly plated with copper whilst contained in the electrochemical cell with the solid electrolyte, $Rb_4Cu_{16}I_7Cl_{13}$, with the aim of saturating the material with copper. A total of 44 mg Cu was plated on the sample. It was examined on removal from the cell, and it was found that the end of the pellet which had been in contact with the solid electrolyte had cracked and splayed out as if an impact had occurred on its end. This may be a result of forcing excess copper into the lattice. A sample from the interior of the pellet was dissolved, and analysed, giving a concentration of 3.35 mg Cu/g bismuth telluride. X-ray powder diffractometry of the interior of the pellet showed only bismuth telluride indicating that the copper in the centre was intercalated copper.

3.3. Activity measurements

The e.m.f. across a cell with pure copper on one side and a sintered pellet of bismuth telluride on the other was allowed to stabilize at 423 K. After approximately 48 h the e.m.f. was 263 mV, corresponding to a copper activity of 0.000 73; and the e.m.f. was increasing at a rate of $1\,\mathrm{mV\,h^{-1}}$. The cell was then allowed to discharge in series with a $3.3\,\mathrm{k\Omega}$ resistor for 9 h. The voltage across the cell reached a steady value, which was approximately 26 mV. The voltage trace on discharge is shown in Fig. 4. The stepped trace and the change in slope may indicate that two reactions occur during discharge at the bismuth telluride electrolyte interface. One reaction is almost certainly the deposition of copper, the second may be the intercalation of copper, as it is unlikely that a two-phase region could form when so little copper had been plated on the specimen.

When the resistor was removed, putting the cell into open circuit mode, the e.m.f. across the cell asymptotically approached a steady value as the copper at the bismuth telluride–electrolyte interface diffused

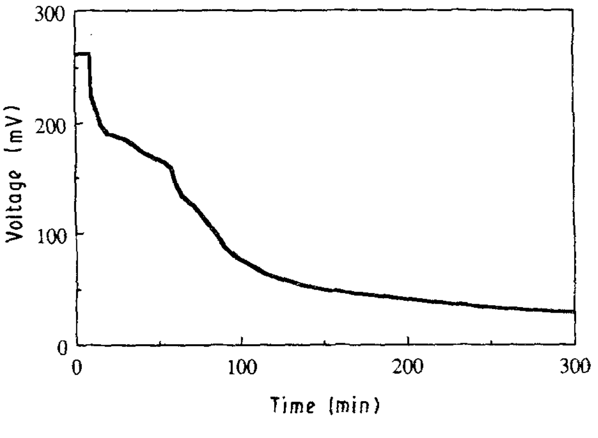

Figure 4 First discharge trace from galvanic cell.

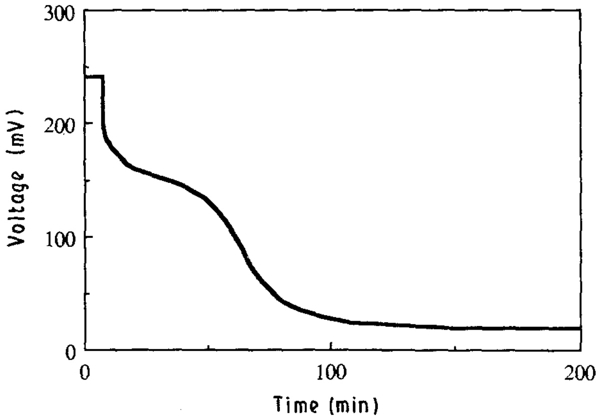

Figure 5 Second discharge curve from galvanic cell.

into the bismuth telluride. After about 24 h the e.m.f. was only increasing very slowly, and had reached a value of 235 mV, corresponding to a copper activity of 0.0016. The e.m.f. was slightly lower than the initial e.m.f., corresponding to an increased activity of copper in the bismuth telluride, and therefore an increased concentration of copper. The cell was then allowed to discharge again for 3 h with a charge of approximately 0.324 C being transferred. The discharge trace is shown in Fig. 5. Again, a stepped trace was obtained with a steady voltage of approximately 20 mV. After the circuit was opened, the cell e.m.f. returned to 233 mV in about 24 h, with the e.m.f. very slowly increasing. This e.m.f. was very slightly lower than the value obtained after the previous discharge, corresponding to a slightly higher copper concentration in the bismuth telluride.

3.4. Potential applied across the cell

Starting with a fresh sintered pellet, the cell was allowed to reach equilibrium without current passing, at a temperature of 483 K. The cell e.m.f. was 275 mV, corresponding to a copper activity in bismuth telluride of 0.001 35. A potential was then applied across the cell and charge forced across the electrolyte. After 10 C had been passed the circuit was broken and the cell voltage was recorded as the cell reapproached equilibrium. The trace obtained is shown in Fig. 6. An initial e.m.f. of 0 V would be expected if pure copper was present at the bismuth telluride–electrolyte interface immediately after passing current. However, it was impossible to record the cell voltage at the instant of switching off the applied potential as a finite time was required to switch the electrical connections. Also, the IR drop component of the cell voltage would take a finite time to relax after breaking the circuit. As can be seen in Fig. 6 the cell voltage increased slowly over time, finally approaching a steady value. The potential continued to increase at a slow rate of about 1 mV h^{-1} and showed no signs of tailing off after 18 h. At this stage the bismuth telluride had probably not been saturated with copper, and the copper was continuing to diffuse into the material from the interface, so reducing the excess at the interface, and decreasing the copper activity at this point. The copper activity after 18 h was about 0.015.

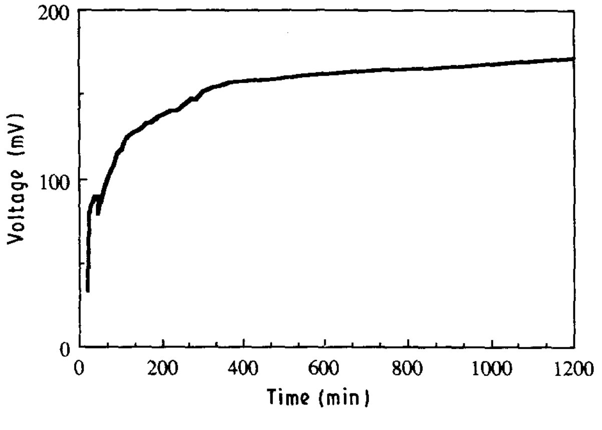

Figure 6 Re-equilibration trace for electrochemical cell.

An effective diffusion coefficient for copper in the polycrystalline bismuth telluride can be calculated from the e.m.f. values shown in Fig. 6. If it is assumed that the e.m.f. changes with time due to the decreasing activity of copper at the bismuth telluride–electrolyte interface, because the copper is diffusing into the bulk of the bismuth telluride, and that the diffusion approximates that of a plane source in one direction with a constant diffusion coefficient, then the concentration distribution is given by [11]

$$C_{\mathrm{Cu}} = \frac{M}{(\pi D_{\mathrm{Cu}} t)^{1/2}} \exp - \left(\frac{x^2}{4 D_{\mathrm{Cu}} t} \right) \tag{4}$$

where C_{Cu} is the copper concentration distribution, M is the number of moles of copper diffusing per unit area, D_{Cu} is the effective diffusion coefficient, x is the distance the copper diffuses, and t is the time. Assuming that the material obeys Henry's law, the copper activity is given by

$$\begin{aligned} a_{\mathrm{Cu}} &= \gamma X_{\mathrm{Cu}} \\ &= \beta C_{\mathrm{Cu}} \end{aligned} \tag{5}$$

where a_{Cu} is the copper activity, γ is the copper activity coefficient, X_{Cu} is the copper mole fraction, and β is a conversion factor relating the copper distribution to the copper mole fraction and activity coefficient. The copper activity can be calculated from the cell e.m.f. Substitution into the diffusion equation results in the expression

$$\ln\left[\left(\frac{\pi D_{\mathrm{Cu}}}{M^2 \beta^2} \right)^{1/2} a_{\mathrm{Cu}} t^{1/2} \right] = - \frac{x^2}{4 D_{\mathrm{Cu}} t} \tag{6}$$

Thus, a plot of $\ln(a_{\mathrm{Cu}} t^{1/2})$ versus $1/t$ will have a slope of $-x^2/4D_{\mathrm{Cu}}$: and the effective diffusion coefficient can be calculated from the slope. A plot for data from Fig. 6 is shown in Fig. 7 along with the linear least squares fit. From the slope of the linear least squares fit to the activity data, which was 992 s, and the length of the bismuth telluride pellet, which was 0.4 cm, the resulting effective diffusion coefficient was 4×10^{-5} cm^2 s^{-1}. This value is in good agreement with the value of 2.19×10^{-5} cm^2 s^{-1} of Carlson [6] for the copper diffusion coefficient parallel to the cleavage planes of large crystallite bismuth telluride.

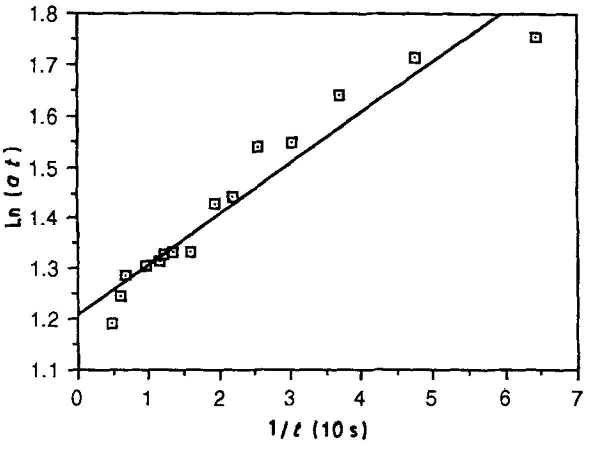

Figure 7 Plot of copper activities as a function of time from the voltage measurement of the solid electrolyte cell after a small charge was passed.

A potential difference was then applied again across the solid electrolyte cell until 10 C charge had been passed. The cell voltage was then monitored as the system returned to equilibrium. A similar shaped trace was obtained to the previous equilibration, except that after 10–12 h the voltage reached a constant level of about 132 mV and did not increase any further. The above procedure was repeated twice more, and on each occasion a steady potential of about 130 mV was reached after some hours. This corresponds to a copper activity of 0.044. This can be compared with a value of 0.042 for the activity of copper given by the thermodynamics for the reaction

$$6Cu + Bi_2Te_3 = 3Cu_2Te + 2Bi \qquad (7)$$

assuming that the activities of the tellurides and bismuth are unity [12]. Thus, the activity probably corresponds to saturation of the bismuth telluride with intercalated copper and the formation of a separate phase of copper telluride (Cu_2Te). To support this view, an X-ray powder diffractometry run on powder from the bismuth telluride–electrolyte interface showed copper telluride (Cu_2Te) present as a major phase.

In summary, it appears that the intercalation of copper into bismuth telluride consists of two processes: the simple diffusion of copper into the material, and the formation of a two-phase region, one of those phases being copper telluride. Saturation of the bismuth telluride and the formation of copper telluride during electroplating with an applied potential difference across the cell occurs after 10–20 C charge (6–12 mg Cu) had been passed, for a bismuth telluride sample weighing 1 g. Interestingly, the amount of copper removed from bismuth telluride by acid leaching was, in general, in the range 2–6 mg, confirming the above observations.

It can be seen that although the activity of copper in bismuth telluride is quite low, the solubility of copper in bismuth telluride is also low.

4. Conclusions

It has been verified that copper is readily intercalated into bismuth telluride. Bismuth telluride can accommodate up to ~ 3 mg Cu/g bismuth telluride as an intercalated species. Additional copper reacts to form the compound copper telluride (Cu_2Te).

Intercalated copper can be removed by a hydrochloric acid leach, but some copper is left in the material, probably copper present as copper telluride. Any excess bismuth in the material is dissolved during the first acid leach, and thereafter the plating, annealing and leaching cycle can be repeated with little further loss of bismuth.

Some copper can also be removed by an electrochemical leach. At the applied currents used in these experiments some bismuth was also dissolved. However, it is possible that a controlled potential electrochemical leach could be used to remove intercalated copper without the dissolution of bismuth telluride.

E.m.f. measurements from a solid, copper-ion conducting electrolyte cell illustrated the two processes of copper deposition and copper intercalation occurring when copper was plated on to bismuth telluride galvanically through the solid electrolyte. The activity of copper in bismuth telluride samples was ~ 0.001. This low activity should allow copper present as an impurity in solder, etc., to readily diffuse into bismuth telluride. An effective diffusion coefficient of 4×10^{-5} cm^2 s^{-1} was measured for copper diffusing into a sintered polycrystalline pellet at 483 K.

References

1. H. J. GOLDSMID and R. W. DOUGLAS, *Brit. J. Appl. Phys.* **5** (1954) 386.
2. M. HANSEN, in "The Constitution of Binary Alloys" (McGraw-Hill, New York, 1958) p. 339.
3. H. J. GOLDSMID, in "Materials Used in Semiconductor Devices", edited by C. A. Hogarth (Wiley, New York, 1965) p. 165.
4. J. D. SMITH, in "The Chemistry of Arsenic, Antimony and Bismuth" (Pergamon Press, Oxford, 1973) p. 612.
5. C. H. L. GOODMAN Jr, *Crystal Growth* **75** (1986) 1.
6. R. O. CARLSON, *J. Phys. Chem. Solids* **13** (1960) 65.
7. M. C. CELIK and D. J. FRAY, *Trans. Inst. Min. Metall.* **91** (1982) C171.
8. R. W. HARDEMAN and D. J. FRAY, *Mater. Sci. Technol.* **4** (1988) 745.
9. Goodfellows Metals, Certificate of Analysis.
10. W. R. GEORGE, R. SHARPLES and J. E. THOMPSON, *Proc. Phys. Soc.* **74** (1959) 768.
11. J. CRANK, in "The Mathematics of Diffusion" (University Press, Oxford, 1956) p. 11.
12. I. BARIN, O. KNACKE and O. KUBASCHEWSKI, in "Thermodynamic Properties of Inorganic Substances" (Springer Verlag, Berlin, 1977) p. 96.

Received 8 May
and accepted 17 May 1991