

ACCELERATED LIFE TEST FOR THERMOELECTRIC JUNCTIONS: SOLDER ELEMENT INTERACTIONS

David D. Allred* and On Van Nguyen†

*Dept of Physics and Astronomy, Brigham Young University, Provo, UT 84604

†512 Claeser Dr., Milpitas, CA 95035

Abstract

A variety of accelerated life tests have been developed for V-VI thermoelectric junctions. Experiments have been performed and interpreted via the Arrhenius equation which allows the interdiffusion of bismuth into thermoelectrics to be extrapolated over a wide temperature range. This technique can be used for other thermoelectric/junction combinations. Techniques for studying barrier layers thermoelectric interactions are also enumerated.

I. Introduction

The purpose of this paper is to begin establishing a taxonomy of failures observed in thermoelectric materials and devices based on V_2VI_3 compounds. The V_2VI_3 compounds are often referred to as simply V-VI compounds or the bismuth telluride family. The specific failures described are related to aging and, particularly, thermal induced changes. Accelerated lifetime tests (ALT tests), particularly those between the thermoelectric and its environment, especially its contacts, are an emphasis of this study. Various ALT tests will be mentioned. The focus here will be on tests relevant to devices containing solders or brazes. In particular interactions between the solder and the thermoelectric will be noted.

The limit of accelerated testing is also noted. The ALT approach is based on various kinetic models such as the Arrhenius equation and the Avrami equation (1,2). Various nonkinetic or discontinuous events; such as solder melting, barriers fracturing, or delaminating from the thermoelectric and the like, can limit the maximum temperature which can be used for certain tests and may constitute an important limit to the maximum temperature even for short times to which devices can be exposed in processing or use.

Understanding the interactions in thermoelectric devices is of vital importance to manufacturers and users alike in reliability assurance and product improvement. The largest current use of V_2VI_3 compounds in thermoelectricity is in Peltier coolers. This work is relevant to the application in determining the likely effects of aging, storage, shipping, and processing requirements of certain users. There are also application of such materials in power generation devices (3) particularly in obtaining electrical power from the catalytically combustion of gas. For the purpose of investigating device failure the interaction of materials and devices with environment can be divided into these classes, which can be considered in order of increasing complexity:

1. Thermoelectric materials at elevated temperatures
2. Thermoelectric material with contact metals including solders
3. Barriers
4. Element/barrier interactions
5. Solder on barrier coated elements
6. Solder/element/strap
7. Complete devices

The specific concerns of this report are solder metals in contact with thermoelectrics (item 2) and element/barrier interactions (item 4).

II. The Problem

Bismuth telluride family of thermoelectric materials are narrow-gap, high-mobility semiconductors. They are low melting (temperatures $\approx 600^\circ\text{C}$) and their free energy of formation is also only modestly negative, less than ~ 20 kcal/mole (1 eV) (4). Thus the formation of the thermoelectric from their constituent elements is only weakly spontaneous and these materials are thus capable of reacting with elements such as lead, tin and indium which form tellurides possessing a more negative free energy of formation than the V-VI's. These elements are common constituents of solders (5).

The free energy of reaction of various V-VI compounds is shown in Ref. 4. It should be noted that even when a reaction is spontaneous it will occur only as fast as kinetically allowed. This is particularly true of solid state reactions. The purpose of this study is to investigate the kinetics of reaction.

III. Solder Element Tests

A. Experimental

Crystals of p-doped $(\text{Bi,Sb})_2\text{Te}_3$ and n-doped $\text{Bi}_2(\text{Te,Se})_3$ were grown by the vertical Bridgeman process (3). The ratio of bismuth to antimony in the p-type was approximately one to three which the ratio of tellurium to selenium in the n-type varied from between 4 to 1 and 9 to 1 depending on application. These were sliced perpendicular to the axis of growth to

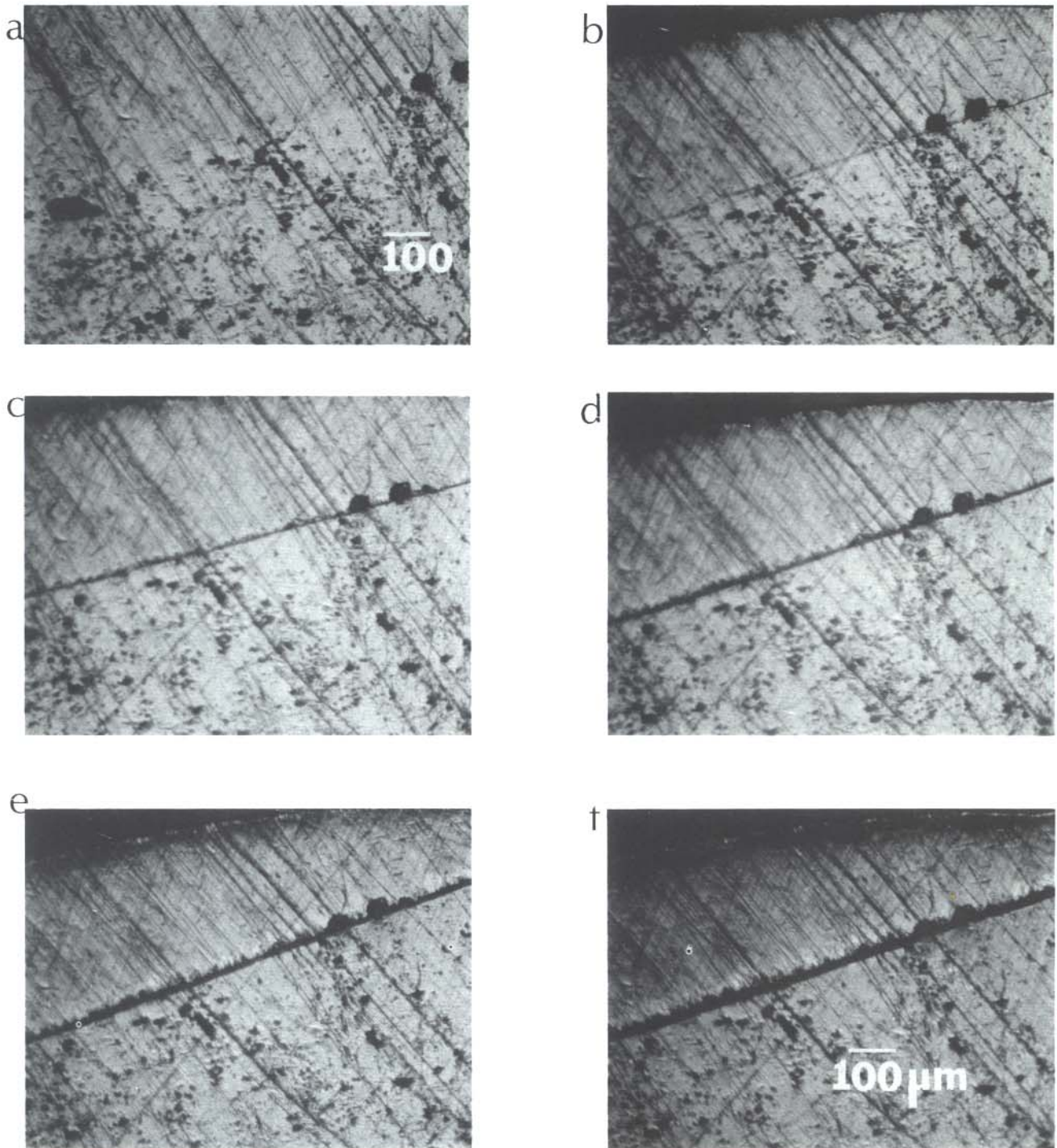


Figure 1. Reaction of bismuth with p type V-IV thermoelectrics at 200°C. Figure a-f are respectively, 0, 1, 10, 30, 70, and 158 min. The reaction zone appears as a dark line or band. Note that the direction the reaction band moves relative to the interface at time = 0 into the bismuth.

prepare a crystal approximately 1 mm thick and 2 to 6 mm in diameter. Sintered pressed powder n and p compacts of similar compositions and dimensions were also obtained (6). Bismuth was applied as a solder to one of the surfaces largely covering it to produce a metallic dome in contact with the thermoelectric. The solder and element were cut in half perpendicular to the soldered surface with a diamond saw—and polished to a smooth, high reflectance finish. Frequently potting, or casting in a metallographic or polishing waxes, was employed to stabilize the element and aid in handling the element during cutting and polishing. Wax, when used, was removed prior to tests.

After the sample was cut and polished the side opposite to the polished surface was rough polished to make it parallel with the first. This facilitated reflection illumination and viewing of the top surface in the microscope. For the initial stages of thermal treatment (up to several hours) the sample was placed polished surface up in a Mettler hot stage mounted on the viewing plane of an Olympus Vanox microscope and was top illuminated. The microscope was equipped with a long working distance objective. The hot stage was fitted with flowing gas for environmental control. This was usually N_2 but forming gas, 3% H_2 in N_2 , was also used. The temperature in the hot stage was controlled and the temperature of the sample mentioned with an independent thermocouple in a few cases to calibrate the hot stage to establish the time it took for samples to heat up. Temperatures could be controlled to a precision ± 0.5 K and an accuracy of ± 1.0 K. The width of interdiffusion and other microscopic distances were measured approximately in situ using a calibrated reticule eyepiece and accurately by measuring distances on polaroid microphotographs taken periodically and measured in the course of the experiment.

Normally the sample was loaded when the hot stage was at temperatures with the cover gas purging the system at a high rate. After the sample was placed in the cell and the cover glass replaced the flow rate was turned down to achieve satisfactory temperature uniformity. If heat treatments larger than a few hours were required, the sample was removed from the hot stage and placed in a controlled ambient (nonoxidizing gas flow) furnace for the required time before returning it to the microscope for observation.

B. Results

In the hot stage the reaction of the bismuth contact solder and thermoelectric are clearly visible. The evidence of the reaction is normal seen as a dark band which grows between the solder and the thermoelectric element (see Figure 1). The band forms immediately when the sample is heated and grows wider with time. Figure 2 is a plot of the width of the reaction band as a function of time for several different temperatures. The rate a width the band grows diminishing slowly with time, as is qualitative consistent with diffusion limited reaction. The band appears dark because the surface of the reacted region is no longer smooth. In fact it may swell slightly (4-7 μm) upwards over the width of a 30 to 40 μm reaction band. The height above the polished surface was determined microscopically after the hot stage experiment. The depth of focus was sufficiently narrow with the 40X plano objective that the relative height between closely separated features could be determined to about 0.3 μm precision. The highest portion was near the free bismuth solder side for both n and p powder pressed elements.

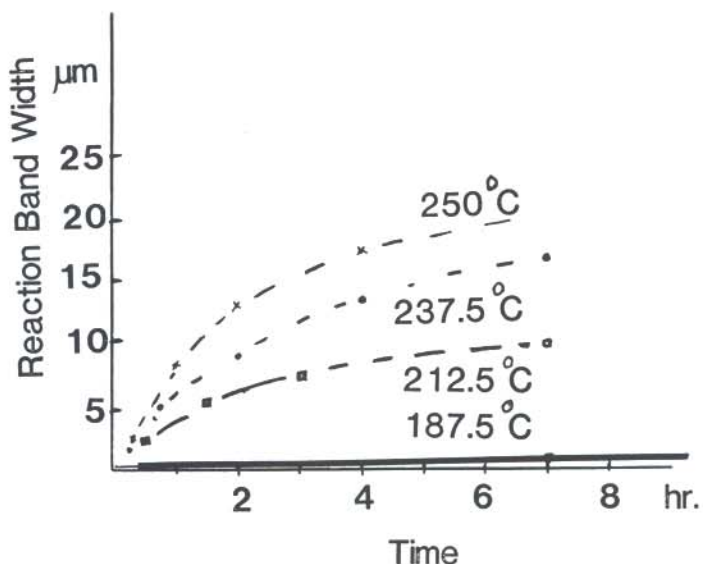


Figure 2. Width of the reaction band as a function of time at various temperatures.

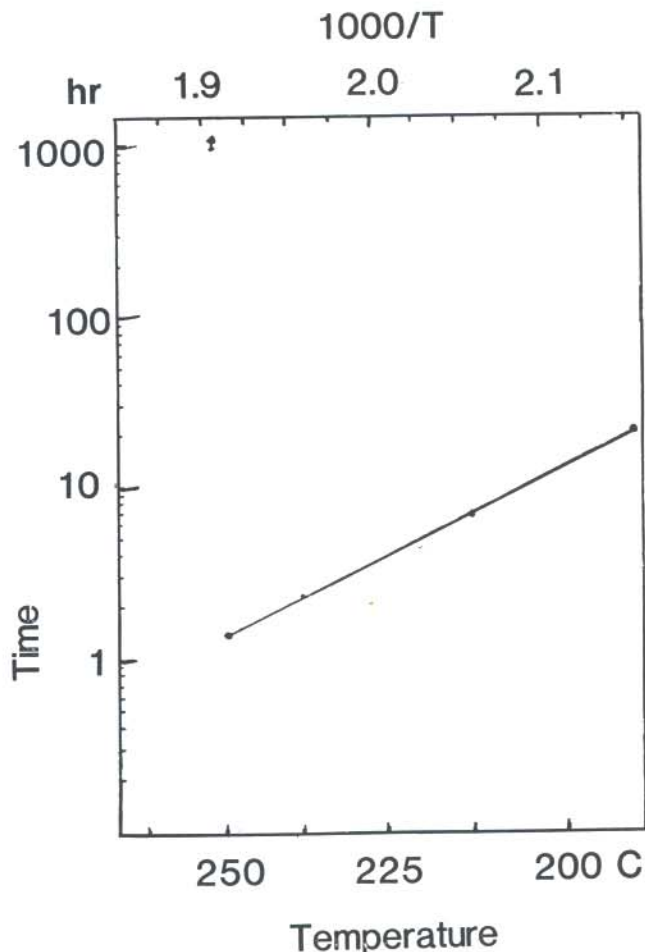


Figure 3. Plot of the logarithm of reaction time vs the reciprocal of absolute temperature. The reaction time is the time required for the Bi/crystalline $Sb_{1.5}Bi_{1.5}Te_3$ reaction band to reach a width of 15 μm at each temperature.

The data of Figure 2 can be analyzed to determine the effect of temperature on the interdiffusion of contact and thermoelectric element. Arrhenius argued nearly a century ago that a reasonable equation for the variation of a rate constant, K , with temperature, T , might be:

$$\ln K = \frac{-E}{RT} + \text{a constant.}$$

where E is a energy termed the activation energy. This equation is termed the Arrhenius equation and can be applied to solid state diffusion and reactions. Since time is inversely related to rate it follows that a plot of the logarithm of the time (log time) required to achieve a given interdiffusion width plotted against the reciprocal of the absolute temperature ($1/T$) should be a straight line. Figure 3 is such a plot for Bi on p-type powder pressed and sintered material. Extrapolating diffusion to low temperatures can indicate the anticipated longterm stability of bismuth, and hence bismuth containing solders, in contact with V-VI thermoelectrics.

The hot stage and polished samples could be used to address a key question in diffusion; that is, whether the bismuth atoms diffuse faster into the thermoelectric or vice versa. From a gross perspective the dome of solder slumps and appears to soak into the body of the thermoelectric. The question is best addressed, however, from a microscopic point of view. One way to do this is to use the location of the surface of the sample opposite the solder as a reference. In this way it was observed that after 1 hr at 250° C the dominate direction of movement is the bismuth unto the sample for both p and n powder pressed samples. For the p element of the current study, for example, the distance between the bismuth solder side of the reaction band and the back of the thermoelectric sample remains fixed at 960 μm while the width of the band increases from 41 to 53 μm . That this is also the dominant direction of movement in n-type samples can also be seen in Figure 4. Along a small portion of the Bi/n-type material interface no reaction occurs. This acts as a marker (of the initial position of the interfaces). The relative position of the marker to the band indicates that the reaction zone consumes the solder, rather than the elements by about three to one.

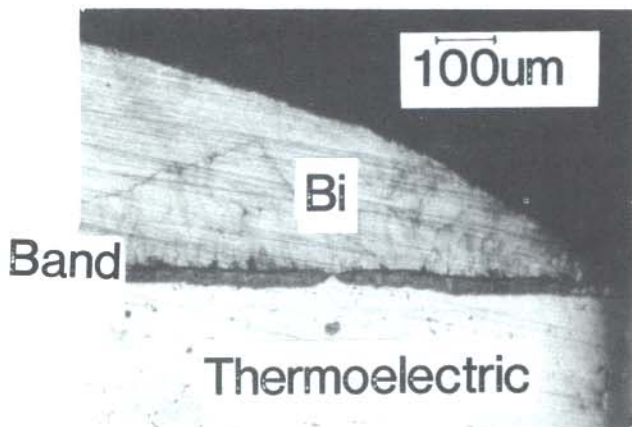


Figure 4. Micrograph of reaction of Bi with powder pressed, n-type V-IV. 250°C 1 hr. Note zone of no reaction along dark reaction band. Reaction band, labelled BAND, has preferential consumed the thermoelectric.

At 200°C, however, band moved almost entirely toward the bismuth. This can be seen in Figure 1. Polishing features on the surface of the thermoelectric keep the same approximate relative distance from the near interface. It appears that the movement of atoms from the thermoelectric into the bismuth is relatively more important at 200°C than it was at 250°C.

The reaction between the solder and the thermoelectric element which can be observed takes place along a free surface. A priori, there is the possibility that diffusion takes place at a different rate than in the bulk of the sample. To test this theory several samples were removed from the hot stage in the middle of the experiment and were sectioned and polished perpendicular to the first cut. The thickness of the reaction band inside the sample could be measured and compared with the free surface. In all cases so examined the thickness of the reaction layer was the same on both free and internal surfaces.

IV. Barrier Layer Tests

A number of barrier layer tests were also devised. These fell into either of two categories. Diffusion and/or volatilization of Te and Se or diffusion/reaction between the barrier and the V-VI compound.

X-ray diffraction was useful in marking the presence and growth of any compounds or phases involving barriers but the technique was time consuming. Optical monitoring of surface darkening could be correlated with compound growth and provided a better control.

Copper is darkened by tellurium and selenium and copper foil in close proximity to the barrier coated thermoelectric proved to be an excellent indicator of incomplete or missing barriers. These techniques will be summarized elsewhere.

Acknowledgments

We gratefully acknowledge the additional assistance of Rea Newell in producing this manuscript.

REFERENCES

1. See a basic text on chemical kinetics such as Walter J. Moore, *Physical Chemistry*, (Prentice-Hall, Inc., Englewood Cliffs, NJ 1963; 3rd Edition) pp. 273-274.
2. J.W. Christian, *The Theory of Transformations in Metals and Alloys* (Pergamon Press, New York, 1965) Ch. 12.
3. On Van Nguyen, David D. Allred and Stanford R. Ovshinsky, "A new multiphase thermoelectric material for power generation," *Proceedings of the Sixth International Conference on Thermoelectric Energy Conversion*, (Univ. of Texas, Arlington, TX March 12-14, 1986) pp. 157-61.
4. Thomas B. Read, *Free Energy of Formation of Binary Compounds: An Atlas of Charts for High-Temperature Chemical Calculations*, (The MIT Press Cambridge, Massachusetts, 1971) pp. 12-13.
5. Howard Manko, *Solders and Soldering*, (McGraw Hill; NY, 1980, 2nd Edition).
6. T.S. Jayadev, et. al., US Patent #4,588,520, "Powder pressed thermoelectric materials and method of making same."