Chemical Stability of (Ag,Cu)$_2$Se: a Historical Overview

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Recent work on Cu$_{2-x}$Se has caused strong interest in this material due to its high reported peak zT (1.5) and the reduction of thermal conductivity through the mechanism of liquid-like suppression of heat capacity. In the 1960s, 3M patented Cu$_{1.97}$Ag$_{0.03}$Se as "TPM-217." Over the following decade it was tested and developed by the 3M Corporation, at the National Aeronautics and Space Administration (NASA) Jet Propulsion Laboratory, Teledyne Energy Systems, and the General Atomics Corporation for use as a next-generation thermoelectric material. During these tests, extreme problems with material loss through Se vaporization and chemical reactions between the material and the device contacts were found. These problems were especially severe while operating under conditions of high iL/A. As a result, the material system was abandoned. The results of these reports are discussed. A simple test of degradation of Cu$_2$Se under conditions of applied current and thermal gradient was performed and showed results compatible with the work done by General Atomics.

INTRODUCTION

Copper(I) selenide is a mixed ion–electron conductor. In addition to being a heavily doped p-type semiconductor, it also shows significant conduction of mobile Cu$^+$ ions ($\sigma_{Cu} \approx 1\,\Omega^{-1}\,m^{-1}$).[1] At 410 K it undergoes a fast-ion phase transition, which causes its ion conductivity to jump dramatically ($to\,\sigma_{Cu} \approx 1000\,\Omega^{-1}\,m^{-1}$).[2] Fast-ion conductors behave as though one of their sublattices has melted, meaning that they exhibit certain liquid-like properties despite being mechanically solid.[3] The heat capacity for a liquid is $3R$ at its melting point, equal to that of a solid in the Dulong–Petit limit, but decreases steadily to $2R$ as the temperature is increased.[4] This reduction is due to transverse phonon modes being suppressed by fast relaxation time. This characteristic has been observed recently in Cu$_2$Se and consequently explains this material's relatively low thermal conductivity and zT = 1.5 at 1000 K.[5] This discovery opens up a new means to improve thermoelectrics; however, questions remain regarding whether it can be successfully integrated into a viable thermoelectric module.

In the late 1960s the 3M Corporation designed and patented a set of highly efficient selenide thermoelectric materials to be used for the next generation of radioisotope thermal generators (RTGs) and other US Department of Energy (DOE) applications.[6] The n-type material developed was based on Gd$_2$Se$_{3-x}$. The p-type material was Cu$_{1.97}$Ag$_{0.03}$Se$_{1+y}$ with $y < 0.01$.[7] This proprietary material was referred to as TPM-217. 3M's reports indicated good thermoelectric properties that were stable over 4000 h, though typically the material would take several hundred hours to become stable.[6] Further material studies were done by the General Atomics Corporation[13–16] and NASA Jet Propulsion Laboratory (JPL).[17–20] Device and generator development was done by 3M and Teledyne Energy Systems.[21] General Atomics images of the material as synthesized by 3M showed clear Cu- and Ag-rich regions, which could be eliminated by further hot-pressing and annealing of the material.[8] The 3M reports also indicated that there was a small problem of Cu extrusion at the interface between the Cu$_{1.97}$Ag$_{0.03}$Se$_{1+y}$ and the cold-side end-cap,[6] and systematic

problems with increasing contact resistances under extended operation.[9]

Data from 3M indicate that $Cu_{1.97}Ag_{0.03}Se_{1+y}$ has a peak zT of 1.2 at 1000 K[9] (Fig. 1). 3M typically synthesized 0.1% excess selenium samples. Data from JPL indicated a peak zT of 0.8 at 800 K. JPL bonded their samples to copper at the cold end. Therefore, the equilibrium Se excess in their samples varied from 0.02% to 0.08% depending on the temperature.[19] Electrical conductivity and thermopower were measured via a four-point technique. Thermal conductivity was directly measured by steady-state direct
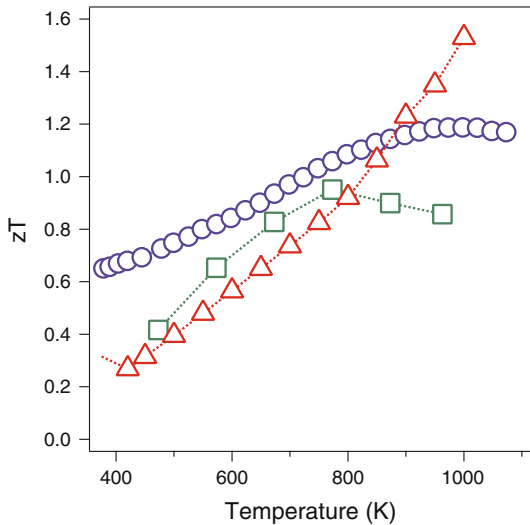
calorimetry,[10] rather than by separate measurement of thermal diffusivity and heat capacity. The material was also evaluated over a 10-year period by the General Atomics Corporation. Most of the information in these reports relates to $Cu_{1.97}Ag_{0.03}Se_{1+y}$ in a device setting, with particular focus on high-temperature (1000 K to 1200 K) stability and operation under typical device thermal gradients with a cold side at 400 K to 600 K and a hot side at 1000 K to 1200 K, as well as under conditions of applied current and in segmented legs and devices. These tests revealed problems that were not reported in the $Cu_{1.97}Ag_{0.03}Se_{1+y}$ original material testing at 3M.

The biggest problem observed was the material loss rate (Fig. 2). At 1200 K the loss rate was found to be $10^{-4}\,g\,cm^{-2}\,h^{-1}$,, and under conditions of applied current the loss rate was measured as high as $10^{-2}\,g\,cm^{-2}\,h^{-1}$ at $iL/A = 8.6$ A/cm.[11] For a reasonable sample geometry, these loss rates would cause rapid deterioration of the material. The mechanism for this loss was believed to be evaporation of Se at the cold end.[9] As thermal and electrical potential gradients created a Cu concentration gradient with a low concentration of copper at the hot end, the Se activity increased, thereby increasing its vapor pressure. The evaporation of selenium causes solid-state precipitation of copper. Under conditions of applied thermal and electrical gradients, it was found that the percent excess selenium in the material varied with temperature. 3M and JPL found that the excess selenium percent increased by a factor of $0.0095\frac{iL}{A}$ over the zero-current concentration, where $\frac{iL}{A}$ is in units of A/cm. To mitigate this problem the p-leg was partitioned with a diffusion barrier. This diminished the problem of Se evaporation but also decreased zT by 25%.[19]

Fig. 1. zT data for $Cu_{1.97}Ag_{0.03}Se$ (TPM-217) as extracted from JPL status reports. Blue circles are data from 3M Corporation tests. Green squares are data from JPL tests.[8] Red triangles represent data from Liu et al.[5]
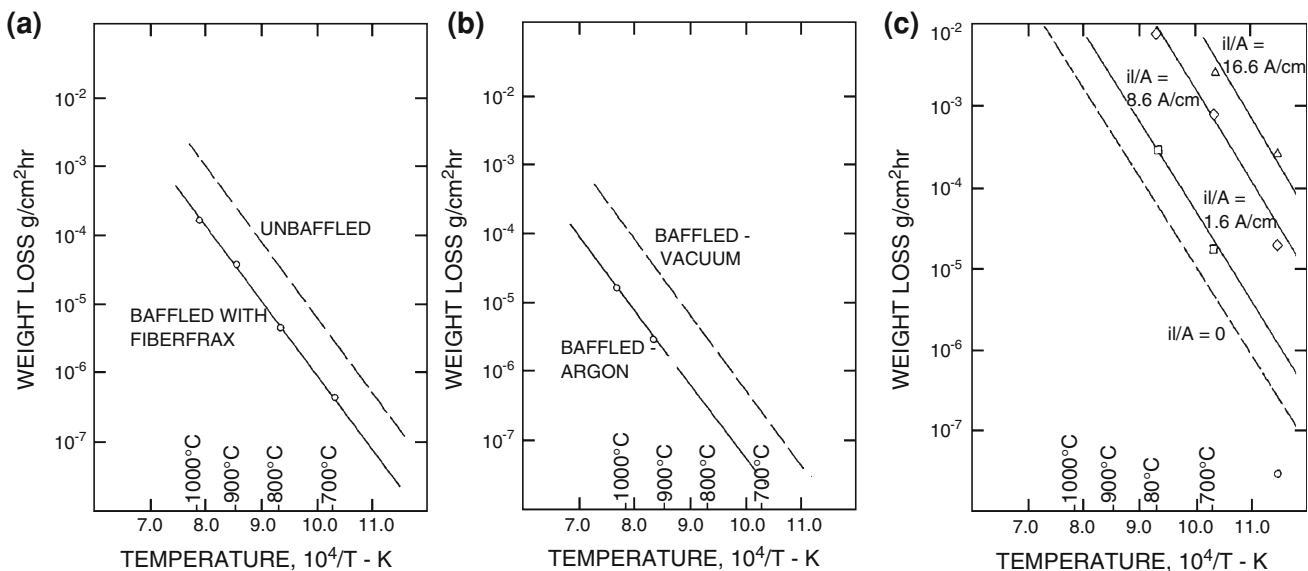

Fig. 2. Weight loss rates for TPM-217 as a function of temperature. Figures 6, 7 and 8 from Ref. 17. (a) Comparison between unprotected and baffled TPM-217. (b) Comparison between TPM-217 in vacuum and in 750 mbar argon atmosphere. (c) Loss rates at different applied currents. II/A ranges from 0 A/cm to 16.6 A/cm.
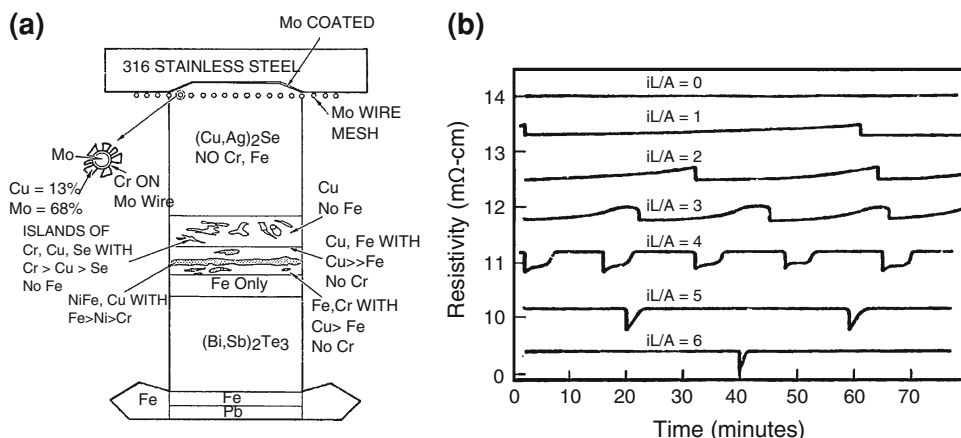
Fig. 3. Degradation of segmented modules. Data from General Atomics final report,[15] representing Fig. 2-21 and Fig. 2-31. (a) Depiction of chemical degradation after isothermal test of *p*-type leg after 2490 h at a 1027 K/380 K thermal gradient. (b) Depiction of resistivity "ratcheting" under conditions of applied current. *iL/A* is in units of A/cm. T_h = 1023 K, T_c = 473 K.
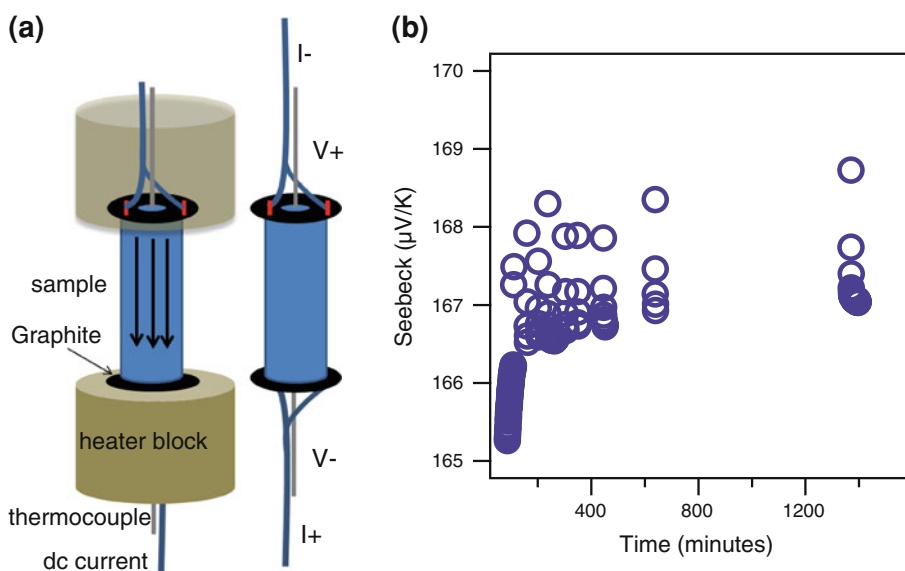

Fig. 4. (a) Thermopower measurement apparatus with modification to allow operation with applied current. Conductive graphite contacts are used for the current source and sink. (b) Seebeck coefficient stability during measurement of sample under conditions of applied current and temperature gradient. It is unclear whether the transients represent instrument error or relaxation of the concentration gradient produced by turning off the current source immediately before the measurement.

To address this issue, General Atomics developed systems to suppress the evaporation of Se. They would baffle the $Cu_{1.97}Ag_{0.03}Se_{1+y}$ with boron nitride and boron oxide glassy coatings.[12] With greater baffling thickness, they found a reduction in the material loss rate of up to two orders of magnitude. The baffling decreases device efficiency by acting as a thermal short. This provides a limiting condition on the thickness of the baffling that can be effectively added to the module. They further found that they could suppress the weight loss rate by one order of magnitude if they operated in a thin (2.5 torr) atmosphere of argon instead of vacuum.[12]

The second major problem was chemical degradation of the material and device, particularly under conditions of applied current. In the original 3M studies, these effects were obscured by the use of Cu as hot- and cold-side contacts. General Atomics found that, at elevated temperature, the Cu in $Cu_{1.97}Ag_{0.03}Se_{1+y}$ would react with the Fe in 316 stainless-steel contacts.[12] Tungsten, molybdenum, and tungsten-rhenium were found to be chemically unreactive to $Cu_{1.97}Ag_{0.03}Se_{1+y}$. However, these materials showed a coefficient of thermal expansion one-fifth that of $Cu_{1.97}Ag_{0.03}Se_{1+y}$, resulting in microcracks through which Cu could diffuse at elevated temperatures.[12] It is also possible that these cracks were related to the approximately 1.4% volume expansion at the 410 K phase transition of the material.[22] In the final General Atomic tests during
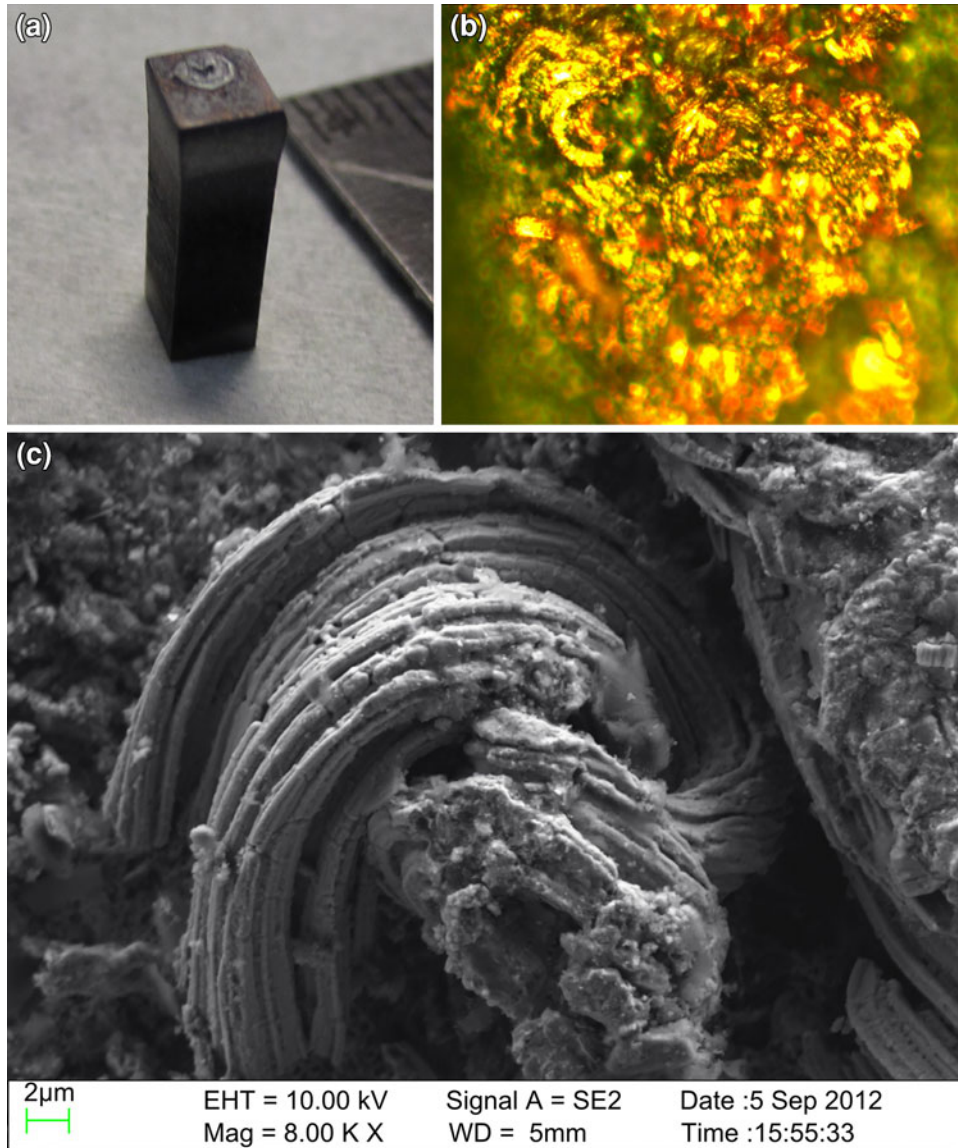
Fig. 5. (a) Sample after applying current for 24 h. (b) Optical microscopy image of the current-sink face of the sample after applying a current for 24 h. Copper can be clearly seen precipitated on the surface. (c) SEM micrograph of top surface of sample after applying current for 24 h. The electromigrated copper grows into nanowire bundles ("whiskers").

the late 1970s, $Cu_{1.97}Ag_{0.03}Se_{1+y}$ was used as the low-temperature segment. Fe was used as the diffusion barrier for the segmented tests, because it was known to be compatible with $(Bi,Sb)_2Te_3$.[9] During isothermal tests it was found that the Fe reacted with the Cu in $Cu_{1.97}Ag_{0.03}Se_{1+y}$ (Fig. 3a). A region of mixed Cu and Fe was found in between the $Cu_{1.97}Ag_{0.03}Se_{1+y}$ and the Fe, as well as a region of $Cu_{1.97}Ag_{0.03}Se_{1+y}$ with inclusions of Cu, Fe, and Cr from the coating of the 316 stainless-steel end caps. Under conditions of applied current these segments failed dramatically. At different values of Il/A ranging from 0 A/cm to 6 A/cm the segments were measured to have resistivity ranging from 15 mΩ cm to 9 mΩ cm when $T_h = 1023$ K and $T_c = 473$ K. The measured Seebeck coefficient and electrical resistivity would also show "ratcheting" behavior: at

regular intervals the transport quantity would suddenly increase for a short period of time and then decrease down to the baseline (Fig. 3b). The ratcheting frequency depended on the applied current but was typically on the order of one ratchet per 15 min. These results were interpreted as due to an irregular electrochemical process. After these tests, the selenide RTG project was terminated.[9] Work done at 3M indicated that, under accelerated conditions ($Il/A = 15$ A/cm), contact resistance increased to up to 700% of leg resistance after 100 h. Upon thermal cycling, the device returned to its original contact resistance.

To understand these results and test their applicability to stoichiometric Cu_2Se, we performed a short electromigration experiment. A piece of copper selenide with cross-sectional area of 11.47 mm² and

length of 10.7 mm was placed in a modified Seebeck apparatus (Fig. 4a). This Seebeck apparatus allows for simultaneous measurement of voltage and temperature and application of current of up to 10 A. The sample was placed under a thermal gradient of 275 K for 16 h with T_h = 795 K and T_c = 520 K. The sample was not visibly affected. The current was varied from 0 A to 10 A under the same thermal gradient as before. The resistivity did not depend upon the applied current, in contradiction to the General Atomics reports.[15] The sample was then run under the same temperature gradient and in current continuously for 24 h. The magnitude of this current was such that the voltage it induced was half the thermoelectric voltage. The direction was such that it transported Cu$^+$ in the direction opposite to thermal diffusion; Cu$^+$ should electromigrate to the hot side and thermally diffuse to the cold side. The applied current was 1 A. The applied current density was j = 9 A/cm. There was no noticeable degradation of the average Seebeck coefficient over this period (Fig. 4b), which is consistent with the reports by JPL, 3M, and General Atomics. When the sample was removed, visual inspection showed that it had undergone deformation at the hot end. Copper residue was visible on the face that had been against the hot-side heater and the current sink. The copper residue was inspected via optical microscopy (Fig. 5a, b) and scanning electron microscopy (SEM, Fig. 5c). The nonuniformity of the surface copper may have been due to spatial inhomogeneity in the contact resistivity between the current electrodes and the sample face. The SEM image reveals that the copper grows as bundles of nanowires. The result is a clear indication that electromigration drives physical degradation of Cu$_2$Se.

It has yet to be shown that liquid-like thermoelectrics based on fast-ion conductors can be used effectively in thermoelectric devices. The historical work by General Atomics, the 3M Corporation, Teledyne Energy Systems, and the NASA Jet Propulsion Laboratory gives reason to be cautious in assuming that the excellent material properties observed in Cu$_2$Se will necessarily lead to a high-quality thermoelectric module. There were three major problems observed. The first was an electrochemical process resulting in weight loss via selenium evaporation. The 3M and General Atomics reports indicate that this problem was solved via baffling of the thermoelectric leg and operation in an argon atmosphere. JPL and Teledyne expressed skepticism that the problem had been sufficiently reduced to prevent mechanical degradation of the thermoelectric generator. The second major problem was that of chemical reactivity at high temperature. In the view of all four major organizations involved in this work, this problem was never solved. Changes in contact resistance over time due to a chemical process at the interfaces between (Ag,Cu)$_2$Se and diffusion barriers and bond pads led to unacceptable degradation of overall module performance. This last problem appears to be the principle reason why the program was cancelled in 1979.

If Cu$_2$Se is to be used in thermoelectric generators, these problems must be solved or evaded. Possible solutions would be the development and use of different diffusion barriers and contact materials, and the operation of the material only at lower temperature. The authors' own work shows that physical degradation of Cu$_2$Se can be induced with currents similar to those needed to build a practical thermoelectric generator.

ACKNOWLEDGEMENTS

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