Direct recovery of metallic tellurium from spent Bi–Te intermetallic alloy

Ryo SASAI1,2,†, Takuya FUJIMURA1 and Takuya SANO3

1Graduate School of Natural Science and Technology, Shimane University, 1060 Nishi-Kawatsu-cho, Matsue 690–8501, Japan
2Next-Generation Tatara Co-Creation Centre (NEXTA), Shimane University, 1060 Nishi-Kawatsu-cho, Matsue 690–8501, Japan
3ARBIZ Corporation, 1–4–2 Showa-machi, Minato-ku, Nagoya 455–0026, Japan

With its low abundance in the Earth’s crust and high mining costs, metallic tellurium (Te) is a limited resource. In advanced material industries, it is irrecoverable from solid wastes. Hence, we investigated the hydrothermal treatment of a Bi–Te intermetallic alloy (BT-alloy) to develop an eco-friendly resource recovery technique for recovering metallic Te. High-purity (≈100 mass %) metallic Te powder can be directly recovered from BT-alloy powder (0.1 g) with H2SO4 solution (30 mL, 3.0 mol/L) at 200 °C for at least 20 h. With H2SO4 and heating, metallic Te was formed by the oxidation of Te2– in the BT-alloy. In this study, we demonstrated for the first time that selective metal deposition by elemental extraction and oxidation from solid materials could be achieved with hydrothermal treatment. Therefore, hydrothermal resource recovery could be used to recover chemical resources, such as metals, directly from solid waste materials.

Key-words : Bi–Te intermetallic alloy, Metallic tellurium, Liquid-solid reaction, Hydrothermal treatment, Resource recovery

1. Introduction

Tellurium (Te) is a non-ferrous metal with limited usage and a low recycle rate owing to its low abundance in the Earth’s crust as well as high mining and refining costs. Te is indispensable in advanced materials used in the steel, glass, electronics, and rubber industries. Considering Japan’s current reliance on the import of various resources, it is essential to establish systems for recovering wasted resources such as spent products and manufacturing wastes, to ensure the availability of critical materials. International studies reporting the research and development of technologies for recovering valuable resources include investigations of Te recovery. However, most of these studies have focused on the development of techniques for recovering Te from the refining slime of Cu or Bi.1–4 Balva et al. reported that a spent Peltier thermoelectric device could be considered as a Cu ore because of its Bi, Sb, and Te concentrations, which are higher than those in natural minerals.5 Most of the manufactured Peltier thermoelectric devices are currently only used for maintenance-free power sources and small in-vehicle refrigerators. However, with the expansion of demand for wireless sensors for IoT and the growing demand for thermal energy recovery power generation from low-temperature exhaust heat to realize SDGs, the market for Peltier thermoelectric devices is expected to grow to about 80 billion yen in 2022.6 Along with such an increase in demand, it is also expected that a large amount of manufacturing waste and waste products will be discarded. However, they did not present a resource recovery technique for obtaining Te from the spent Peltier device. Meanwhile, Bahrami et al. reviewed on the recycling of thermoelectric materials.7 In this review, the suitable recycling way of the waste of Bi–Te intermetallic alloy, which were discharged during the mechanical processing of the ingot, by Tritt’s group8),9) and Fan group10) was introduced. In their techniques, waste was recycled as Bi2Te3 ingot by alkali metal method under hydrothermal conditions. However, these techniques can only recover raw materials for thermoelectric material such as Bi2Te3. Thus, the recovery of each element such as Bi and Te from the spent thermoelectric materials was also introduced in this review. Lee et al. reported that Bi2Te3 and metallic Te powders could be collected by treating the spent thermoelectric material by hydrazine hydrate solution.13,14) Moreover, So et al. reported that metallic Bi and Te powders could be recovered by the hydrazine reduction treatment under appropriate pH conditions, respectively.15) Their hydrazine reduction method is inexpensive and effective as a resource recovery method from the spent thermoelectric material. However, it is necessarily the most suitable method because it requires a harmful and dangerous chemical reagent as hydrazine.

† Corresponding author: R. Sasai; E-mail: rsasai@rko.shimane-u.ac.jp
We have been investigating resource recovery from various types of solid wastes, such as cemented carbide cermets\textsuperscript{16,17} and Nd–Fe–B permanent magnets\textsuperscript{18} via eco-friendly hydrothermal methods. The hydrothermal treatment of WC–Co cermet using nitric acid containing a small amount of hydrofluoric acid at temperatures below 200 °C revealed that a high-purity WO$_3$ crystalline powder could be selectively obtained with a W yield of 100 mass \%\textsuperscript{16,17}. Moreover, rare-earth elements (Nd and Dy) in Nd–Fe–B permanent magnets could be recovered as high-purity oxalate salts (~100 mass \%) via a hydrothermal treatment with a mixed solution of hydrochloric and oxalic acids at 110 °C\textsuperscript{18}. Thus, hydrothermal treatment using an appropriate reagent is a promising and eco-friendly resource recovery technique that can be applied to various types of solid waste. In this study, we investigated the hydrothermal treatment of a spent Bi–Te intermetallic alloy (BT-alloy), which is applied as a semiconductor in Peltier and thermoelectric conversion devices, using sulfuric acid (H$_2$SO$_4$) solutions of different concentrations.

2. Materials and methods

2.1 Materials

We used a spent BT-alloy with the following chemical composition: Bi, 357.3 ± 0.6 mg/g; Te, 500.3 ± 0.7 mg/g; and Sb, 141.5 ± 0.8 mg/g. In this alloy, Sb, also a valuable resource, served as the hole dopant to provide p-type semiconducting properties. As is well known, Bi$_2$Te$_3$ shows a crystal structure in which Bi layers and Te layers are alternately stacked, and the Sb is doped in a part of Bi sites. The oxidation state of Bi and Sb are +3, and that of Te is −2. The BT-alloy was ground in a mortar, and the obtained powder was used as the sample for the hydrothermal resource recovery measurements.

2.2 Hydrothermal experiment for metallic Te recovery from spent Bi–Te intermetallic alloy with H$_2$SO$_4$

The hydrothermal treatments of the BT-alloy powder with H$_2$SO$_4$ were conducted by applying the following procedure: (1) BT-alloy powder (0.1–0.3 g) was sealed in a pressure vessel lined with a polyfluoro-resin with H$_2$SO$_4$ (30 mL, 0.5–3.0 mol/L). (2) The pressure vessel was placed in an oven set at a given temperature (100–200 °C) for a specified treatment time (1–20 h). (3) Both the liquid and precipitated solid obtained were collected via filtration under reduced pressure. (4) After rinsing with H$_2$SO$_4$, the collected solid precipitate was dried at 60 °C under reduced pressure.

2.3 Characterization

The quantitative analysis of the metals (Bi, Te, and Sb) in each collected liquid after the specified treatment was performed via inductively coupled plasma-atomatic emission spectroscopy (Optima 2000DV, PerkinElmer Co., Ltd.). From this elemental analysis, the extraction rate ($E$) of the hydrothermal treatment was calculated as follows:

\[
E = \frac{m_{\text{liquid}}}{m_{\text{total}}} \times 100 \text{ (mass \%)} \quad (1)
\]

where $m_{\text{liquid}}$ and $m_{\text{total}}$ are the weights of a given metal in the collected liquid and BT-alloy powder, respectively. Here, the experimental errors were approximately 1% of the $E$ value. The collected precipitated solids were identified by X-ray diffraction (XRD) analysis (MiniFlex-II, RIGAKU Corporation) using Ni-filtered Cu Kα radiation (30 kV and 15 mA).

3. Results and discussion

3.1 Metallic Te recovery from spent Bi–Te intermetallic alloy through hydrothermal treatment with H$_2$SO$_4$

Figure 1 presents the treatment-time dependence of the $E$ value of each metal when the hydrothermal treatment was conducted in 3.0 mol/L H$_2$SO$_4$ at different temperatures (°C): 100 = □, 120 = ○, 140 = △, 160 = ▽, 180 = ◇, and 200 = ◢.
conducted in 3.0 mol/L H$_2$SO$_4$ at different temperatures. The $E$ values of both Bi and Sb increase with an increase in treatment time and temperature, reaching approximately 100 mass % at 200 °C in 20 h. This result indicates that it takes a relatively long treatment time to dissolve Bi and Sb elements in BT-alloy powder. This would suggest that the dissolution reaction of Bi and Sb cannot be explained by dissolution in H$_2$SO$_4$. Concurrently, the $E$ value of Te is nearly 0 mass %, irrespective of the temperature and treatment time. These experimental findings strongly indicate that hydrothermal treatment with H$_2$SO$_4$ is an effective method for selectively recovering Te as a precipitate from the BT-alloy powder. Similar experiments were conducted at 25 °C (BT-alloy powder: 0.1 g, H$_2$SO$_4$ concentration ([H$_2$SO$_4$]): 3.0 mol/L, H$_2$SO$_4$ volume: 100 mL, treatment time: 20 h); however, the dissolution of Bi, Sb, and Te could not be observed. Thus, this extraction behavior can only be realized under these hydrothermal conditions.

Figure 2 displays the XRD pattern of the solid precipitate collected at 200 °C after 20 h of treatment. All diffraction peaks can be ascribed to metallic Te. Here, the broad diffraction peak observed in the low angle region (2θ = 10 ~ 40°) is from the glass substrate for XRD measurement. Unexpectedly, the hydrothermal treatment with H$_2$SO$_4$ resulted in the direct and complete separation and recovery of metallic Te from a BT-alloy powder with approximately 100 mass % purity. As a result of ICP-AES analysis of nitric acid (0.1 mol/L), in which the collected solid precipitate was completely dissolved, no element other than Te could be confirmed. Therefore, this result also indicates that the purity of the recovered metallic Te was almost 100 mass %.

The dependence of the $E$ value on [H$_2$SO$_4$] is shown in Fig. 3. For Te, the $E$ value is independent of [H$_2$SO$_4$] and approximately 0 mass %. In comparison, the $E$ values of both Bi and Sb increase with the rising [H$_2$SO$_4$], reaching approximately 100 mass %. Thus, [H$_2$SO$_4$] should be at least 3.0 mol/L.

The $E$ values are plotted against the weight of the BT-alloy powder in Fig. 4. Regardless of the weight change, the $E$ values for Bi and Te are constant at approximately 100 and 0 mass %, respectively. Concurrently, the $E$ value of Sb decreases with the increase in the weight of the BT-alloy powder. This experimental finding indicates that the dissolution reaction of Sb is inhibited when the amount of the BT-alloy powder is increased within the weight range considered in this study. Only the diffraction lines of metallic Te can be observed in the XRD pattern of the solid precipitate collected under 0.3 g BT-alloy powder, and crystalline Sb compounds are not observed. This result may be due to the low solubility of amorphous Sb compounds such as oxides and sulfates produced under the present hydrothermal conditions. Therefore, the optimal sample weight of the BT-alloy powder is determined to be less than 0.1 g per 100 mL H$_2$SO$_4$ (3.0 mol/L).

3.2 Selective formation mechanism of metallic Te under hydrothermal conditions with H$_2$SO$_4$

In this study, we demonstrated that the hydrothermal treatment of the selected BT-alloy powder with H$_2$SO$_4$...
could directly yield metallic Te powder. However, the dissolution behavior of each element was not observed during the hydrothermal treatment at 25 ºC under the following conditions: 0.1 g sample weight, 0.3 mol/L [H₂SO₄], and 20 h treatment time [E = 6.5 (Bi), 5.2 (Sb), and 3.1 (Te) mass %]. These results indicate that hydrothermal conditions are essential for the direct recovery of metallic Te powder. In the BT-alloy compound, Bi and Sb are present as Bi³⁺ and Sb³⁺, respectively, whereas Te exists as Te²⁻. It is generally easy to dissolve both Bi³⁺ and Sb³⁺ in acids under heating. However, even with heating, Te²⁻ barely dissolves in H₂SO₄. H₂SO₄ is known to act as an oxidized agent under heating (SO₄²⁻ + 2H₂O). Thus, Te²⁻ ions in the BT-alloy compound were oxidized by the oxidation action of H₂SO₄ to form metallic Te (Te²⁻ → Te + 2e⁻). Based on these observations, it can be inferred that metallic Te powder was selectively and directly precipitated under these hydrothermal conditions.

4. Conclusion

We conducted the hydrothermal treatment of a BT-alloy powder with H₂SO₄ as the reaction solution. High-purity metallic Te powder (~100 mass %) could be directly recovered from the BT-alloy powder. The optimal hydrothermal conditions were as follows: [H₂SO₄] = 3.0 mol/L, sample weight = 0.1 g, volume of reaction solution = 30 mL, treatment temperature = 200 ºC, and treatment time ≥ 20 h. Moreover, the following formation mechanism of metallic Te was suggested: (1) accelerated dissolution of both Bi and Sb in the BT-alloy compound by H₂SO₄ under hydrothermal conditions, and (2) oxidation of Te²⁻ in the BT-alloy compound to metallic Te by H₂SO₄ as the reducing reagent. The results of this study demonstrate the effectiveness of hydrothermal treatment with H₂SO₄ as a Te recovery method for the spent BT-alloy powder for the first time. From this study, it was clarified that hydrothermal treatment can selectively metallize a valuable target element in solid wastes. However, since this paper is a laboratory-scale experiment, there are several problems that must be solved such as acid corrosion of hydrothermal container and wastewater treatment, in order to construct a practical process using the present technique, that is, the hydrothermal metallization method. To solve these problems, we will need to study a method with high efficiency for separating and recovering Bi and Sb in the wastewater and lowering the treatment temperature for hydrothermal metallization. Moreover, if these problems can be solved, the present technique could become one of practical techniques for recovering metallic Te from Peltier thermoelectric devices.

Acknowledgements The authors are grateful to ARBIZ Corporation for donating the spent Bi–Te intermetallic alloy. This work was partly supported by the Exploratory Research of the Next-Generation Tatara Co-Creation Centre (NEXTA), Shimane University. We would like to thank Editage (www.editage.com) for English language editing.

References
1) T. Shibasaki, K. Abe and H. Takeuchi, Hydrometallurgy, 29, 399–412 (1992).
2) J. E. Hoffman, J. Miner. Met. Mater. Soc., 41, 33–38 (1989).
3) K. I. Rhee, C. K. Lee, Y. C. Ha, G. J. Jeong, H. S. Kim and H. J. Sohn, Hydrometallurgy, 53, 189–201 (1999).
4) X. Guo, Z. Xu, D. Li, Q. Tian, R. Xu and Z. Zhang, Hydrometallurgy, 171, 355–361 (2017).
5) M. Balya, S. Legeai, L. Garoux, N. Leclere and E. Meux, Environ. Tech., 38, 791–797 (2017).
6) https://www.offgridenergyindependence.com/articles/4631/thermoelectric-generators-a-750-million-market-by-2022 (access date: 2020/11/29).
7) A. Bahrami, G. Schierning and K. Nielsen, Adv. Energy Mater., 10, 1904159 (2020).
8) X. Ji, J. He, X. Ji, N. Gothard and T. M. Tritt, J. Appl. Phys., 104, 034907 (2008).
9) Z. Su, J. He, X. Ji, N. Gothard and T. M. Tritt, Sci. Adv. Mater., 3, 596–601 (2011).
10) X. Fan, X. Z. Cai, X. W. Han, C. C. Zhang, Z. Z. Rong, F. Yang and G. Q. Li, J. Solid State Chem., 233, 186–193 (2016).
11) Q. Xiang, X. Fan, X. Han, C. Zhang, J. Hu, B. Feng, C. Jiang, G. Li, Y. Li and Z. He, Mater. Chem. Phys., 201, 57–62 (2017).
12) Q. Xiang, X. A. Fan, X. Han, C. Zhang, J. Hu, B. Feng, C. Jiang, G. Li, Y. Li and Z. He, J. Phys. Chem. Solids, 111, 34–40 (2017).
13) K.-J. Lee, Y.-H. Jin and M.-S. Kong, J. Nanosci. Nanotechnol., 14, 7919–7922 (2014).
14) B. Swain and K.-J. Lee, J. Chem. Technol. Biotechnol., 92, 614–622 (2017).
15) H. So, J. Yoo, K. Ryu, M. Yang and K.-J. Lee, Ceram. Int., 45, 7226–7231 (2019).
16) N. F. Gao, R. Sasai, H. Itoh and Y. Suzumura, J. Ceram. Soc. Jpn., 112, S1387–S1392 (2004).
17) T. Kojima, T. Shimizu, R. Sasai and H. Itoh, J. Mater. Sci., 40, 5167–5172 (2005).
18) T. Itakura, R. Sasai and H. Itoh, J. Alloy. Compd., 408, 1382–1385 (2006).