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Thermal Decomposition of Thermoelectric Material $CoSb_3$: A Thermogravimetry Kinetic Analysis

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The thermal decomposition of the thermoelectric $CoSb_3$ alloy was investigated using thermogravimetry (TG). TG curves obtained in inert gas flow with different heating rates were used to perform kinetic analysis based on the Arrhenius equation. Kinetic parameters, such as the effective activation energy, the pre-exponential factor, and the kinetic model function $f(\alpha)$, were obtained using the Freeman–Carroll method, the multiheating rates method, and the Coats–Redfern equation. The activation energy was found to be around 200 kJ/mol, and the reaction mechanism for the decomposition of $CoSb_3$ alloy mostly obeys the second-order chemical decomposition process $f(\alpha) = (1-\alpha)^2$.

Key words: Thermoelectric materials, decomposition, thermal analysis, kinetic models

INTRODUCTION

During the last two decades, thermoelectric materials have attracted renewed interest due to their important applications in fields such as power generation from waste heat or solid-state Peltier cooling.[1] A qualified thermoelectric material should have a high figure of merit value defined by $ZT = S^2\sigma T/\kappa$, where S, σ, κ, and T are the Seebeck coefficient, electrical conductivity, thermal conductivity, and absolute temperature, respectively.[2] Among the various thermoelectric materials, the binary skutterudite $CoSb_3$-based alloys have been regarded as potential thermoelectric materials for use at elevated temperatures due to their relatively high ZT values at elevated temperature.[3] To further enhance the figure of merit of $CoSb_3$-based alloys, various ideas and methods have been suggested and investigated, such as filling the interstitial voids in the $CoSb_3$ lattice with rare-earth atoms, element doping or replacement, as well as introduction of nanostructures into $CoSb_3$ samples. These efforts have resulted in favorable results, and $CoSb_3$-based alloys with successively enhanced ZT values have been reported.[4–7]

Besides enhancing the ZT value of $CoSb_3$-based alloys, study of their thermal stability is also an important issue, since these alloys are proposed for use at elevated temperature. There are two main factors which affect the thermal stability of $CoSb_3$-based alloys. One is oxidation of the alloy in air or atmosphere containing oxygen at elevated temperature. Another is sublimation of antimony from the alloy at elevated temperature, resulting in decomposition of the alloy. The oxidation of $CoSb_3$-based alloys has been investigated by several groups.[8–10] It was reported that oxidation of pure $CoSb_3$ samples starts at about 653 K and the oxidation activation energy is about 170 kJ/mol. For element (Fe,Y)-doped $CoSb_3$ alloys, the starting temperature and activation energy of oxidation may be slightly different.

Decomposition of $CoSb_3$-based alloys in vacuum or inert gases has also been studied by researchers. Snyder et al.[11] studied the thermostability of $CoSb_3$ in vacuum at temperatures between 873 K and

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