FEM Analysis on Thermoelectric Properties of Metal/TiO$_{2-x}$ Composites with Random Distribution of Metal Powder

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Abstract: An analysis model of finite element method with a random distribution for thermoelectric composites was built. Thermoelectric properties including electrical resistivity, Seebeck coefficient and thermal conductivity of M/TiO$_{2-x}$ (M = Cu, Ni, 304 stainless steel (304SS)) thermoelectric composites were investigated by the proposed model. Cu/TiO$_{2-x}$ composite showed a large decrease in electrical resistivity while thermal conductivity of 304SS/TiO$_{2-x}$ composite was slightly increased. Calculated dimensionless figure-of-merit, $ZT$ of Ni/TiO$_{2-x}$ composite was higher than those of TiO$_{2-x}$ and the other composites in a wide range of metal volume fractions because Ni has large absolute values of Seebeck coefficient, power factor and dimensionless figure-of-merit compared to the other two metals. It was found that power factor and dimensionless figure-of-merit of thermoelectric composites depended on the balance among electrical resistivity, thermal conductivity and Seebeck coefficient. The results revealed that it is important for M/TiO$_{2-x}$ composites to choose suitable metal additive with high power factor and dimensionless figure-of-merit.

Introduction

Thermoelectric materials have attracted much attention of many researchers as they can directly convert heat energy into electrical energy by Seebeck effect. Hence, they are expected of effective utilization of waste heat. Especially, many researchers have focused on oxide thermoelectric materials because they have many advantages such as non-toxicity, thermal stability, and high oxidation resistance, among others.

The performance of thermoelectric materials is usually evaluated by power factor as follows.

\[ P = \frac{S^2}{\rho} \]  

And/or dimensionless figure-of-merit,

\[ ZT = \frac{T S^2}{\rho \kappa} = \frac{TP}{\kappa} \]  

where $T$ is the absolute temperature, $S$ is the Seebeck coefficient, $\rho$ is the electrical resistivity and $\kappa$ is the thermal conductivity. Thermoelectric materials with high performance need a large $ZT$ value which means a large Seebeck coefficient in absolute value, a low electrical resistivity and a low thermal conductivity. Therefore, metal powder addition into thermoelectric oxides (e.g. Ni/TiO$_{2-x}$, Ag/Ca$_3$Co$_4$O$_9$ and others [1-8]) is generally used to decrease electrical resistivity as one method for performance improvement. Although electrical resistivity of thermoelectric materials can be decreased largely by the metal addition, it is always accompanied with some negative effects such as thermal conductivity increase. Therefore, investigation of the composite effects and their influence on thermoelectric properties is important.
In our previous work, an analysis model of finite element method (FEM) for thermoelectric composites was proposed and established [1]. In that work, the thermoelectric properties and performance were investigated. In the present work, thermoelectric properties of thermoelectric composites with a random distribution of metal powder addition into TiO$_2$ matrix were analyzed by the proposed model. The composite effects on thermoelectric properties and performance were also discussed.

**Construction of FEM Analysis Model for Thermoelectric Composite**

In this work, we focused on thermoelectric composites with the random distribution of metal powder. A FEM model of thermoelectric composite was composed of square areas as shown in Fig. 1. The thermoelectric composite was assumed to be two dimensions with a length, $L$ and a width, $W$. Also, the elements of added metal and the matrix were assumed to be in the same size. The areas of the added metal and matrix were dispersed using [0, 1] random numbers. After that, a uniform pixel FEM mesh with a specified element size was given on the geometric model. In this work, the model size and the square area size given by 200×50 µm and 2×2 µm, respectively. The square area with 2×2 µm in the FEM model is divided into four square elements with eight nodes.

When an electrical potential difference $\Delta V$ and a temperature difference $\Delta T$ were given between the two lines of $X = 0$ and $X = L$ in the model, boundary conditions can be written as

$$V(0) = V + \Delta V, \quad V(L) = V, \quad T(0) = T + \Delta T, \quad T(L) = T.$$  \hspace{1cm} (3)

The electrical resistivity, thermal conductivity, and Seebeck coefficient can be calculated by the following equations

$$\rho = -\frac{\Delta V}{J_{\text{avg}}} \quad \kappa = -\frac{Q_{\text{avg}}}{L\Delta T} \quad S = \frac{V_{\text{avg}}}{\Delta T}$$ \hspace{1cm} (4)

where $J_{\text{avg}}$, $Q_{\text{avg}}$ and $V_{\text{avg}}$ are the average electrical current density, the average heat flux and the average electrical potential on the boundary lines of $X = 0$ or $X = L$, respectively. In this work, an electrical potential difference of 0.1 V and a temperature difference of 6 K were given between the two lines of $X = 0$ and $X = L$ in the model as the boundary conditions. The mean temperature was 373 K.

<table>
<thead>
<tr>
<th>Materials</th>
<th>TiO$_{2-x}$</th>
<th>Cu</th>
<th>Ni</th>
<th>304SS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electrical resistivity, $\rho$ (Ωm)</td>
<td>$9.05 \times 10^{-3}$</td>
<td>$2.23 \times 10^{-8}$</td>
<td>$1.03 \times 10^{-7}$</td>
<td>$7.86 \times 10^{-7}$</td>
</tr>
<tr>
<td>Thermal conductivity, $\kappa$ (W/Km)</td>
<td>$5.42$</td>
<td>$395$</td>
<td>$83$</td>
<td>$15.8$</td>
</tr>
<tr>
<td>Seebeck coefficient, $S$ (µV/K)</td>
<td>$-293$</td>
<td>$2.33$</td>
<td>$-16.8$</td>
<td>$-1.66$</td>
</tr>
<tr>
<td>Power factor, $P$ (W/K$^2$m)</td>
<td>$9.49 \times 10^{-6}$</td>
<td>$2.43 \times 10^{-4}$</td>
<td>$2.74 \times 10^{-3}$</td>
<td>$3.51 \times 10^{-6}$</td>
</tr>
<tr>
<td>Dimensionless figure-of-merit, $ZT$</td>
<td>$6.53 \times 10^{-4}$</td>
<td>$2.30 \times 10^{-4}$</td>
<td>$1.23 \times 10^{-2}$</td>
<td>$8.28 \times 10^{-5}$</td>
</tr>
</tbody>
</table>

$^a$ Reference [1], $^b$ Reference [9], $^c$ Reference [10], $^d$ Reference [11]
Thermoelectric properties of M/TiO$_2$$_x$ (M = Ni, Cu, and 304 stainless steel (304SS)) composites were investigated by the composed model. Thermoelectric properties of the composition materials are shown in Table 1. Cu was chosen because it has a small electrical resistivity than the other metals. Besides, 304SS was chosen as a low thermal conductivity metal and Ni was chosen due to its large absolute value in Seebeck coefficient, power factor and dimensionless figure-of-merit. In this work, ANSYS (Ver.13.0, ANSYS Inc.) was used for the FEM analysis.

Results and Discussion

The relationships between metal volume fraction and the thermoelectric properties of M/TiO$_2$$_x$ composites are shown in Fig. 2. On the whole, the transition trends of each parameter of the composites are plainly influenced by those of each addition metal, thermoelectric properties of M/TiO$_2$$_x$ composites have changes from TiO$_2$$_x$ to each added metal as increasing metal volume fraction. It is found that electrical resistivity and absolute value of Seebeck coefficient of M/TiO$_2$$_x$ composites are decreased remarkably from 40 to 60 vol.% of metal addition. On the other hand, thermal conductivity increases with metal volume fraction.

From Fig. 2 (a), when metal volume fraction is fewer than 50 vol.%, electrical resistivity of composites shows almost the same values for the different metal addition. Effect of metal addition become conspicuous at high metal volume fraction especially above 50 vol.%. Since Cu has
the lowest electrical resistivity of the three metals, Cu/TiO$_{2-x}$ composite shows the lowest electrical resistivity by the composite effect. Besides, electrical resistivity of 304SS/TiO$_{2-x}$ composite is higher than those of the other composites because electrical resistivity of 304SS is greater than the other two metals. For 304SS/TiO$_{2-x}$ composite, it shows the smallest increase of thermal conductivity by metal addition compared to the other metals in Fig. 2 (b). However, Cu/TiO$_{2-x}$ composite shows the largest increase in thermal conductivity among the three composites.

The absolute value of Seebeck coefficient is decreased until 50 vol.% and then keeps very small value near zero as the metals. Especially, in the case of Cu/TiO$_{2-x}$ composite, the Seebeck coefficient has the reversion of positive and negative when the Cu volume fraction locates between 50 to 70 vol.%, in which Seebeck coefficient get values close to zero. It is interesting that the three parameters of the thermoelectric composites have the different point of metal volume fraction, of which has a sudden trend change.

As a result, power factor and dimensionless figure-of-merit in the range from 50 to 70 vol.% are very small as shown in Fig. 3. Power factors of Cu/TiO$_{2-x}$ and Ni/TiO$_{2-x}$ composites show an increasing tendency till 50 vol.% by decreasing electrical resistivity as shown in Fig. 3 (a). However, power factor of 304SS/TiO$_{2-x}$ is decreased because Seebeck coefficient is decreased. Above 50 vol.%, Ni/TiO$_{2-x}$ composite has the highest power factor value, followed by Cu/TiO$_{2-x}$, TiO$_{2-x}$ and finally 304SS/TiO$_{2-x}$.

Dimensionless figure-of-merit of each composite shows a decrease tendency until 50 vol.%; it is saturated to the value of each added metal in the range over 50 vol.% as shown in Fig. 3 (b). Dimensionless figure-of-merits of Cu/TiO$_{2-x}$ and 304SS/TiO$_{2-x}$ composites are lower than that of TiO$_{2-x}$ because dimensionless figure-of-merit of added metal such as Cu and 304SS is lower than those of Ni and TiO$_{2-x}$. It is important to opt for suitable additive metal for thermoelectric composite with high performance.

Conclusions

Thermoelectric properties and performances of M/TiO$_{2-x}$ thermoelectric composites were investigated by FEM analysis model. Electrical resistivity of M/TiO$_{2-x}$, composites was decreased, thermal conductivity of M/TiO$_{2-x}$ composites was increased and Seebeck coefficient of M/TiO$_{2-x}$ composites was lower by metal addition. Power factor and dimensionless figure-of-merit of M/TiO$_{2-x}$ composites can be improved by adding metal with high performance. It is important for M/TiO$_{2-x}$ composites to choose suitable metal additive with high power factor and dimensionless figure-of-merit.

References