Single Thermite-Type Combustion Synthesis of Fe$_2$VAl for Thermoelectric Applications from Fe, V$_2$O$_5$ and Al Powders

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Abstract

Single thermite-type combustion synthesis (STCS) for synthesizing Heusler alloy Fe$_2$VAl from Fe, V$_2$O$_5$, and Al powders for thermoelectric applications was proposed and investigated, in which the microstructure and the thermoelectric properties of the product were mainly examined. Macroscopically, STCS was successfully carried out to produce metallic product of Fe$_2$VAl in lower part and alumina as slag in upper part. According to SEM observation and FE-EPMA-analyzed, elemental mapping images, the product contained dispersed inclusions of spherical Al$_2$O$_3$ with 0.4mol% and angulated AlN with 1.0mol%. In comparison to the reported data on Fe$_2$VAl, the thermal conductivity at room temperature became about half. It could be because of increased phonon scattering due to dispersed AlN&Al$_2$O$_3$ and non-stoichiometry of the product; Fe$_{2.06}$V$_{1.01}$Al$_{0.93}$. As a result, the maximum values for the product were 99.6 $\mu$Wm$^{-1}$K$^{-2}$ in power factor and $2.19 \times 10^{-3}$ at 309 K in dimensionless figure of merit.

Keywords: thermoelectric materials; microstructure; metals and alloys; composite materials
1. Introduction

Thermoelectric properties are typically evaluated by dimensionless figure of merit, ZT. ZT is expressed as follows;

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

where \( Z \) is the figure of merit of a thermoelectric material (K\(^{-1}\)), \( S \) is the Seebeck coefficient (VK\(^{-1}\)), \( T \) is the absolute temperature (K), \( \rho \) is the electrical resistivity (Ωm), and \( \kappa \) is the thermal conductivity (Wm\(^{-1}\)K\(^{-1}\)). It is essential for thermoelectric materials to improve the ZT.

Fe\(_2\)VAl has been known as a thermoelectric material for its unique physical properties. Heusler alloy Fe\(_2\)VAl is a semimetal with a narrow pseudogap at the Fermi level [1, 2]. Small stoichiometric deviations can cause big changes in its transport properties [3]. Two methods for controlling the pseudogap in Fe\(_2\)VAl have been reported by several researchers. One is to change its composition from stoichiometric to nonstoichiometric [3-5], and the other is to substitute a fourth element [6-13]. The methods proposed increase the absolute values of the Seebeck coefficient and reduce the electrical resistivity of Fe\(_2\)VAl [3-13]. However, the thermal conductivity of Fe\(_2\)VAl is comparatively large as a thermoelectric material; about 28 (Wm\(^{-1}\)K\(^{-1}\)) at room temperature, resulting in the small ZT of Fe\(_2\)VAl [14]. For obtaining high-performance Fe\(_2\)VAl, it is essential to decrease its thermal conductivity.

Three processes of Fe\(_2\)VAl fabrication have been conventionally reported. The first one is melting method based on ingot metallurgy [3-6, 8-10], the second one is mechanical alloying [11-13], and the third one is the combination of them [7]. All of the conventional processes require pure V as raw material to synthesize Fe\(_2\)VAl, in which V has been industrially produced by a thermite reaction from V\(_2\)O\(_5\) and Al using strong exothermic reaction. Thermite reactions are reduction reactions of metal oxides using Al as a reduction agent. In these reactions, oxidation of Al to Al\(_2\)O\(_3\) releases a large amount of heat, propagating a rapid combustion wave. The problem is that the large exothermic heat generated is only used for producing V, without any heat recovery. In the thermite reaction of the V production, Al is excessively added to eliminate
unreacted V$_2$O$_5$, resulting in the low purity V product with Al. For purifying the product, electron beam melting with volatilization of Al is necessary [14]. Next, the V obtained is arc-melted or mechanically alloyed with Fe and Al to synthesize Fe$_2$VAI as final product. Thus, for synthesizing Fe$_2$VAI industrially, we concluded that the production method of V has three defects; 1) Exothermic heat from the thermite reaction is not used efficiently. 2) The loss of Al is inevitably accompanied. 3) The following exergy-consuming electron beam melting treatment is needed.

To overcome these drawbacks in the conventional production of Fe$_2$VAI, thermite-type combustion synthesis (TCS), defined as combustion synthesis using thermite reactions from Fe, V$_2$O$_5$ and Al powders, is quite attractive for saving energy and operating time. Excess heat from thermic reaction of Al+V$_2$O$_5$ is reasonably utilized for melting of Fe and excess Al, and for alloying of Fe$_2$VAI without the electron beam melting and the loss of Al (see Fig. 1). In addition, conventional melting requires all the raw materials—Fe, V, and Al—to be pure metals. In contrast, in the proposed process, we can use metal oxide V$_2$O$_5$, which is cheaper and more abundant than V. In addition, TCS for producing Fe$_2$VAI has possibility of improving its ZT. P. Wen et al. reported that the thermal conductivity of CoSb$_3$ was reduced by dispersion of Al$_2$O$_3$, which is a by-product of TCS [15]. If the by-product of Al$_2$O$_3$ can be dispersed in the product Fe$_2$VAI, its thermal conductivity can be reduced, resulting in higher ZT. Therefore, the purpose of this study is to synthesize Heusler alloy Fe$_2$VAI by thermite-type combustion synthesis, in which its microstructure and thermoelectric properties are mainly examined.

We can define “single thermite-type combustion synthesis” (STCS) as a process for synthesizing Fe$_2$VAI via one thermite reaction, in which V$_2$O$_5$ is reduced by Al. Moreover, we can define “double thermite-type combustion synthesis” (DTCS) as a process involving two thermite reactions, in which both Fe$_2$O$_3$ and V$_2$O$_5$ are reduced by Al. However, this paper deals with STCS only and DTCS will be reported elsewhere.
2.Experimental

Commercially available powders of Fe with 99.9% in purity and 3–5 \( \mu \)m in grain size, \( V_2O_5 \) with 99.99% in purity and 75 \( \mu \)m in grain size, and Al with 99.99% in purity and 3 \( \mu \)m in grain size were used for preparing the samples studied here. The powders were weighed according to the stoichiometry of Eq. (3) and were then mixed in an alumina tumbling ball milling pot, which did not contain any balls to prevent the powders adhering to the inside wall. The milling pot was operated at 100 rpm for 3.6 ks in air. The resulting mixture was then placed in a graphite crucible. A carbon foil igniter was placed on the powders. Finally, the powders were electrically flashed at room temperature for about 10 s. The STCS-synthesized (STCSed) products were homogenized at 1273 K for 172.8 ks in an Ar atmosphere. The phase composition and morphology of the products were determined and analyzed by using an X-ray diffractometer (Miniflex, Rigaku, Tokyo, Japan) and field emission electron probe micro analyzer (FE-EPMA) (JXA-8530F, JEOL, Tokyo, Japan). The STCSed samples were cut to predefined forms. The electrical resistivity and Seebeck coefficient of the samples were measured using a Seebeck coefficient/electrical resistance measurement system (ZEM-3, ULVAC-RIKO, Yokohama, Japan) from room temperature to 873 K in a He atmosphere. The thermal conductivity of the sample was measured by a laser flash thermal constant analyzer (TC-7000, ULVAC-RIKO, Yokohama, Japan) from room temperature to 873 K in vacuum.
3. Results and Discussions

STCS consists of an exothermic reaction (1) and an alloying reaction (2), given below:

\[
\begin{align*}
\frac{1}{2} V_2O_5 + \frac{5}{3} Al & \rightarrow V + \frac{5}{6} Al_2O_3 \quad (1) \\
2 Fe + V + Al & \rightarrow Fe_2VAI \\ 
\end{align*}
\]

Reaction (2) can proceed by utilizing the large amount of exothermic heat generated by reaction (1) ($\Delta H = -621 \text{ kJ at 298 K}$). The overall reaction of STCS can be written as follows:

\[
2 Fe + \frac{1}{2} V_2O_5 + \frac{8}{3} Al \rightarrow Fe_2VAI + \frac{5}{6} Al_2O_3 \quad (3)
\]

The theoretical achieving temperature of a combustion synthesis reaction, which is called adiabatic flame temperature, is very important to estimate the state of the products after reaction. The adiabatic flame temperature of the equation (3) was calculated to be 2327 K which was the same as the melting point of Al$_2$O$_3$. From the calculation, we revealed that 60.8% of Al$_2$O$_3$ melted and the rest did not melt. This temperature is higher than the melting point of Fe, V, and Al, showing that Fe, V, and Al were liquid during STCS.

Figure 1 shows the schematic illustrations of the conventional V-production method and the proposed STCS method as heat recovery of the conventional thermite reaction. Fe and Al was also added to the raw materials of the conventional V-production method.

Fig. 2 shows the photographs of the samples placed in a graphite crucible before and after STCS. Before STCS, the color of the raw materials resembled that of ash. After STCS, the ash color of the raw materials disappeared, and products with metallic luster and black color were generated. The raw materials and products were subjected to X-ray diffraction (XRD) measurements, the results of which are shown in Fig. 3. The figure indicates that the metallic luster and black products are Fe$_2$VAI and Al$_2$O$_3$, respectively. The degree of ordering was estimated by reference intensity ratio (RIR) method. Fe$_2$VAI which had ordered L21 structure was about 46.1%, which had BCC structure was about 53.9%. This showed the STCSed Fe$_2$VAI did not have perfectly ordered L21 structure.
Fig. 4 shows a scanning electron microscope (SEM) image and elemental mapping images of the cross-sectional surface of the STCSed and heat-treated product, respectively. The locations at which Al, O, and N were partially richer correspond to the black parts in the SEM image. These black parts indicate that \( \text{Al}_2\text{O}_3 \) and AlN existed partly in the STCSed and heat-treated product. During STCS, the reaction given by Eq. (3) occurred, and the melted products were separated by gravity. The densities of \( \text{Fe}_2\text{VAl} \) and \( \text{Al}_2\text{O}_3 \) are \( 6.60 \times 10^3 \) and \( 3.97 \times 10^3 \) kg m\(^{-3}\), respectively. This implies that \( \text{Fe}_2\text{VAl} \) should be at the bottom of the crucible and \( \text{Al}_2\text{O}_3 \) on top of it. Fig. 2 confirms this as the black product \( (\text{Al}_2\text{O}_3) \) was observed in the upper region of the reactor after STCS and the metallic luster product \( (\text{Fe}_2\text{VAl}) \) was observed in the lower region. However, the products were air-cooled and the \( \text{Fe}_2\text{VAl} \) and \( \text{Al}_2\text{O}_3 \) solidified before they could perfectly separate. This resulted in residual \( \text{Al}_2\text{O}_3 \) in \( \text{Fe}_2\text{VAl} \). AlN could have been produced by the reaction between \( \text{N}_2 \) left in the powders and Al. From the elemental mapping images in Fig. 4, the contained amounts of \( \text{Al}_2\text{O}_3 \) and AlN were estimated to be about 0.4 and 1.0 mol\%, respectively. More detailed SEM image and elemental mapping images of the dotted area of inclusions in Fig. 4 are shown in Fig. 5. The black parts which have circular shape were \( \text{Al}_2\text{O}_3 \) and which have angulated shape were AlN. The reason for the difference in shape between \( \text{Al}_2\text{O}_3 \) and AlN can be considered from the adiabatic flame temperature. The adiabatic flame temperature of the STCS reaction was 2327 K, implying that most part of \( \text{Al}_2\text{O}_3 \) was liquid and AlN was solid. Liquid \( \text{Al}_2\text{O}_3 \) was curled by the effect of surface tension before solidification.

Fig. 6 shows SEM images and elemental mapping images of the matrix part in Fig. 4. In the matrix, we confirmed segregation of V with about 1 \( \mu \text{m} \) in size. Fig. 7 shows SEM images and elemental mapping images of V before and after heat treatment for 48 h at 1273 K. Before the homogenization heat treatment, larger segregation of V was observed in the dotted area in Fig. 7(a) and 7(b). During heat treatment, the larger segregation of V became smaller with the diffusion of V but smaller segregation of V was still left. The melting point of V is 2183 K which is higher than that of Fe (1811 K) and Al (933 K), meaning that it was short time for V to maintain the liquid state and that
diffusion was not enough. In addition, the size of V2O5 was 75 μm which was larger than that of Fe (3–5 μm) and Al (3 μm). This shows that the inside of the product V cannot be diffused completely. To obtain perfectly homogenized Fe2VAI, smaller size V2O5 and longer heat treatment will be needed.

Table 1 Elemental analysis of the matrix part of STCSed and heat-treated Fe2VAI, in which upper, middle and lower parts are corresponded to u, m, and l in Fig. 2.

<table>
<thead>
<tr>
<th>Molar ratio (mol%)</th>
<th>Standard variation (mol%)</th>
</tr>
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<tbody>
<tr>
<td>Fe</td>
<td>V</td>
</tr>
<tr>
<td>Upper part</td>
<td>50.8</td>
</tr>
<tr>
<td>Middle part</td>
<td>51.4</td>
</tr>
<tr>
<td>Lower part</td>
<td>52.3</td>
</tr>
<tr>
<td>Average</td>
<td>51.5</td>
</tr>
</tbody>
</table>

Table 1 shows the results of the quantitative analysis for the matrix part of the STCSed and homogenized Fe2VAI. The quantitative analysis was taken place for upper part, middle part, and lower part, of the matrix part (except Al2O3 and AlN parts) of the STCSed and heat-treated Fe2VAI to research its compositional difference in the different locations. The upper, middle, and lower part were corresponded to u, m, and l in Fig. 2, respectively. Elemental analysis was taken place ten times at every location on the terms of probe diameter of 5 μm. The composition of the STCSed Fe2VAI was almost uniform at every vertical position within the standard variation. The average composition of the STCSed Fe2VAI was 51.5 mol%Fe-25.2 mol%V-23.3 mol%Al (Fe2.06V1.01Al0.93).

The temperature dependence of electrical resistivity, the Seebeck coefficient, the thermal conductivity, the power factor, and the dimensionless figure of merit of the STCSed and heat-treated Fe2VAI, together with the reference data (taken from T. Mori et al.), are shown in Fig. 8 [10]. The electrical resistivity showed a downward slope, which agrees with previous studies [10]. The Seebeck coefficient values were about 10% to 30% smaller than those previously reported [10]. This reduction was attributed
to the small difference in the compositions of STCSed and stoichiometric Fe$_2$VAI. The thermal conductivity at room temperature was about half of that reported in the literature [10]. The reduction of the thermal conductivity is believed to be related to increase of phonon scattering by the increase in grain boundary regions due to dispersed Al$_2$O$_3$ and AlN and the small difference of the composition of the STCSed and heat-treated alloy from stoichiometry. The maximum values of power factor and dimensionless figure of merit were 99.6 $\mu$Wm$^{-1}$K$^{-2}$ and $2.19 \times 10^{-3}$, respectively at 309 K.

This article indicated the possibility of STCS for producing Fe$_2$VAI, however, further improvement in thermoelectric properties are desired. For larger Seebeck coefficient, the segregation of V should be removed by diminishing the grain size of V$_2$O$_5$ and the heat treatment condition should be optimized for obtaining more homogenized and ordered Fe$_2$VAI; and then substitution of a fourth element is needed.
4. Conclusions

(1) Single thermite-type combustion synthesis was successfully carried out to separate metallic part of Fe$_2$VAl as product and alumina part macroscopically due to gravitation.

(2) Microscopically, the product contained inclusions which are 0.4mol%-Al$_2$O$_3$ of circular shape and 1.0mol%-AlN of angulated shape. SEM image and FE-EPMA-analyzed, elemental mapping images showed the V segregation with the size of 1 μm in the matrix part of the product.

(3) The total average composition of the product was Fe$_{2.06}$V$_{1.01}$Al$_{0.93}$ according to elemental analysis.

(4) The thermal conductivity at room temperature was about half of that reported in the literature because of the increase of phonon scattering by the increase in grain boundary regions due to dispersed Al$_2$O$_3$ and AlN and the small difference of the composition of the STCSed and heat-treated alloy from stoichiometry. As a result, the maximum values of the power factor and the dimensionless figure of merit for the STCSed Fe$_2$VAl were 99.6 μWm$^{-1}$K$^{-2}$ and $2.19 \times 10^{-3}$ at 309 K, respectively.
References

Figure captions

Fig. 1 Schematic images (a); the conventional method for producing V by a thermite reaction and (b); the proposed method of producing Fe$_2$VAI directly for improving the conventional method in terms of heat recovery.

Fig. 2 Photographs of the samples (a) before and (b) after single thermite-type combustion synthesis (STCS), in which one end of well-mixed powder of Fe, V$_2$O$_5$, and Al in a vertically-placed graphite crucible were ignited in argon atmosphere with 5N in purity and 0.1MPa in pressure and the lower product had metallic luster; the upper one had black. The points u, m, and l in the lower side are corresponded to upper, middle, and lower part in Table 1, respectively.

Fig. 3 XRD patterns of the raw materials of Fe, Al and V$_2$O$_5$, black product in upper part, and metallic luster product in lower part, demonstrating successful thermite reaction due to gravitational separation.

Fig. 4 Scanning Electron Microscope (SEM) image (a) and FE-EPMA-analyzed, elemental mapping images for element O (b), N (c), Fe (d), V (e), and Al (f) of the STCSed and heat-treated product from Fe: V$_2$O$_5$: Al=2: (1/2): (8/3) in molar basis, in which main product contained AlN or Al$_2$O$_3$ as inclusion of black particle in SEM according to careful observation. Note that dotted area of inclusion has three elements of Al, N and O, which is enlarged for identification of AlN and Al$_2$O$_3$ from shape and element in Fig. 5.

Fig. 5 SEM image (a) of dotted area of inclusion in Fig. 4 and FE-EPMA-analyzed, elemental mapping images for element Al (b), N (c), and O (d) in the matrix of the STCSed and heat-treated product, showing angulated AlN and spherical Al$_2$O$_3$ due to melting.
Fig. 6 SEM image (a) of matrix without inclusion, and FE-EPMA-analyzed, elemental mapping images for element Fe (b), V (c), and Al (d) of the cross-sectional surface of the STCSed and heat-treated product, showing one micrometer in segregation although it was heat-treated at 1273K for 48 hours.

Fig. 7 Effect of heat-treatment on element V; SEM images (a) of product before heat treatment for 48 h at 1273 K, and (c) product after heat treatment, together with FE-EMPA-analyzed, elemental mapping images (b) and (d) for V. Remember that dotted-area of V disappeared by the heat treatment.

Fig. 8 Temperature dependence of the electrical resistivity, the Seebeck coefficient, the thermal conductivity, the power factor, and the dimensionless figure of merit, of the STCSed and heat-treated Fe$_2$VAl, which was actually Fe$_{2.06}$V$_{1.01}$Al$_{0.93}$ according to elemental analysis. Closed point and dotted line as reference are Fe$_2$VAl fabricated by arc melting [10].
A) Conventional

Heater

\[ \text{Mixture of Al & V}_2\text{O}_5 \]

Ignition

\[ \text{V}_2\text{O}_5 + \frac{5}{3}\text{Al} = 2\text{V} + \frac{5}{6}\text{Al}_2\text{O}_3 + 621\text{kJ} \]

\[ T_{ad} = 3418\text{K} \]

Propagation

Completion

Separation

\[ \rightarrow \text{Time} \]

B) Proposed

\[ 2\text{Fe} + \frac{1}{2}\text{V}_2\text{O}_5 + \frac{8}{3}\text{Al} \rightarrow \text{Fe}_2\text{VAI} + \frac{5}{6}\text{Al}_2\text{O}_3 \]

\[ T_{ad} = 2327\text{K} \]

\[ \text{Mixture of Al & V}_2\text{O}_5 \]

\[ \& \text{Fe & Al} \]

Ignition

\[ \rightarrow \text{Propagation} \]

Completion

\[ \text{Al}_2\text{O}_3 \]

\[ \text{Fe}_2\text{VAI} \]

Separation

\[ \rightarrow \text{Time} \]