RMn<sub>2</sub>Si<sub>2</sub> (R = La, Ce, Pr, Nd, Sm, Gd) Compounds Grown from Metal Flux and Properties of the Crystals

Kiyokata IIZUMI, Shigeru OKADA,* Takao MORI,** Toetsu SHISHIDO,*** Kunio KUDOU**** and Peter ROGL*****

Faculty of Engineering, Tokyo Polytechnic University, 1583, Itabashi-ku, Tokyo, 173-8585
*Faculty of Engineering, Kokushikan University, 3-28-1, Setagaya, Setagaya-ku, Tokyo 154-8515
**National Institute for Materials Science, Advanced Materials Laboratory, 1-1, Namiki, Tsukuba-shi 305-0044
***Institute for Materials Research, Tohoku University, 2-1-1, Katahira, Aoba-ku, Sendai-shi 980-0812
****Faculty of Engineering, Kanagawa University, 3-27-1, Rokkakubashi, Kanagawa-ku, Yokohama-shi 221-8686
*****Institut für Physikalische Chemie der Universität Wien, Währingerstrasse 42, A-1090 Wien, Austria

金属フラックスからRMn<sub>2</sub>Si<sub>2</sub>（R = La, Ce, Pr, Nd, Sm, Gd）化合物の育成と結晶の性質

飯泉清賢・岡田 繁氏・森 孝雄氏・宍戸 principales氏・工藤邦男氏・Peter Rogl氏

東京工芸大学工学部ナノ化学科, 243-0297 奈良県高谷山市新栄 1583
*国士舘大学工学部システム工学科, 154-8515 東京都世田谷区世田谷 4-28-1
**材料・材料研究機構無変形研究所, 305-0044 茨城県つくば市京木 1-1
***東北大学金属材料研究所, 980-0812 宮城県仙台市青葉区平 2-1-1
****神奈川大学工学部機械工学科, 221-8686 神奈川県横浜市神奈川区六角橋 3-27-1
*****ウィーン大学物理化学研究所, Währingerstrasse 42, A-1090 Wien, Austria

RMn<sub>2</sub>Si<sub>2</sub> (tetragonal, S.G.: I4/mmm) (R = La, Ce, Pr, Nd, Sm and Gd) crystals were grown from high-temperature lead metal flux by slowly cooling under an argon atmosphere. The RMn<sub>2</sub>Si<sub>2</sub> (R = Ce, Pr, Nd, Sm and Gd) crystals were obtained as thin plates with well-developed [001] faces. The largest crystals have maximum dimensions of approximately 2.3 x 2.3 x 0.02 mm. LaMn<sub>2</sub>Si<sub>2</sub> was generally obtained as a powder of irregular shape. The values of the micro-Vickers hardness for the [001] faces of RMn<sub>2</sub>Si<sub>2</sub> are in the range of 5.8 ± 0.4 to 6.5 ± 0.5 GPa. The oxidation process of RMn<sub>2</sub>Si<sub>2</sub> (R = Ce, Pr, Nd, Sm and Gd) crystals was studied at the temperature below 1473 K by thermogravimetric and differential thermal analyses (TG-DTA). The TG curves show that the oxidation of CeMn<sub>2</sub>Si<sub>2</sub>, PrMn<sub>2</sub>Si<sub>2</sub>, NdMn<sub>2</sub>Si<sub>2</sub>, SmMn<sub>2</sub>Si<sub>2</sub>, GdMn<sub>2</sub>Si<sub>2</sub> crystals start at approximately 738, 979, 999, 784, and 763 K, respectively. The weight gains of the compounds after TG determination were measured to be in the range of 16.4 to 29.2 mass%. The results of magnetic susceptibility measurements agree with recent previous studies on these compounds. [Received November 25, 2003; Accepted February 5, 2004]

Key-words : RMn<sub>2</sub>Si<sub>2</sub> (R = Ce, Pr, Nd, Sm, Gd) crystal, Unit cell parameters, Hardness, Thermal stability, Magnetic susceptibility

1. Introduction

RMn<sub>2</sub>Si<sub>2</sub> (tetragonal, S.G.: I4/mmm) single crystals have attracted considerable interest because of their remarkable properties and potential application as high-temperature thermoelectrics. However, the data available on the properties of RMn<sub>2</sub>Si<sub>2</sub> are in most cases obtained from measurements of polycrystalline samples. Therefore, it is desirable to grow single crystals, to obtain more reliable information on the properties. Ternary rare earth manganese silicides have been synthesized by the solid-state reaction method, arc-melting method and molten metal flux. In this study, we report the experimental conditions for growing relatively large single crystals of RMn<sub>2</sub>Si<sub>2</sub> (R = La, Ce, Pr, Nd, Sm and Gd) from a high-temperature lead flux in an argon atmosphere. La, Ce, Pr, Nd, Sm and Gd are selected as rare earth elements from the light and middle region of the lanthanide series.

These compounds were characterized by micro-Vickers hardness, oxidation resistance heated in air and magnetic susceptibility at low temperatures.

2. Experimental

2.1 Syntheses of crystals

The reagents used to prepare the samples were small pieces of 99.9% rare earth elements (La-Gd), 99.9-99.99% Mn pieces, 99.99%Si powder and 99.99%Pb pieces. The rare earth elements (R = La, Ce, Pr, Nd, Sm and Gd), Mn and Si were mixed together at atomic ratios of R : Mn : Si = 1 : 2 : 2. The amount of Si in the starting materials was fixed at 0.4 g throughout all the experiments. Lead was added to these mixtures at a ratio of 3.8 : 1 in weight. The mixture of starting materials was placed in a high purity (99.9%) BN crucible (20 mm diameter and 30 mm length) together with a BN cover and heated in an Ar atmosphere at 1623 K for 5 h. The solution was cooled to 1073 K at a rate of 50 K h<sup>-1</sup> and then quenched to room temperature. Dissolving the lead in a solution of dilute acetic acid separated the crystals.

2.2 Characterization

The crystal structures and unit cell parameters of the phases were examined by X-ray diffraction (XRD) with monochromatic Cu Kα radiation. Relatively large crystals of RMn<sub>2</sub>Si<sub>2</sub> were selected under a stereomicroscope. The morphology of the crystals was examined using a four-circle diffractometer and scanning electron microscopy (SEM). The chemical composition and impurity of the crystals were analyzed with an electron probe microanalyzer (EPMA) and an energy-dispersive detector (EDX).

The micro-Vickers hardness for the crystals was measured at room temperature in air. A load of 0.49 N was applied for
15 s at approximately four positions on a well-developed (001) plane of each crystal. The obtained values were averaged and the experimental error was estimated.

The oxidation resistance of RMn$_2$Si$_2$ crystals was studied by thermogravimetric and differential thermal analyses (TG–DTA).\textsuperscript{5, 6} Pulverized samples of approximately 20 mg were heated at a rate of 10 K min$^{-1}$ in air.

Magnetic susceptibility of the powder samples of RMn$_2$Si$_2$ was measured using a commercial superconducting quantum interference device (SQUID) magnetometer in the temperature range of 2 K to 300 K.

3. Results and discussion

The XRD evidence for the crystalline phases of RMn$_2$Si$_2$ obtained after reaction is shown Fig. 1. As seen from Fig. 1, for the La–Mn–Si system, LaMn$_2$Si$_2$, MnSi, Mn$_2$Si$_3$, and an unknown phase were obtained, for the Ce–Mn–Si system, CeMn$_2$Si$_2$, MnSi, and an unknown phase were obtained, for the Pr–Mn–Si system, PrMn$_2$Si$_2$ and Mn$_2$Si$_3$ were obtained, for the Nd–Mn–Si and Sm–Mn–Si systems, NdMn$_2$Si$_2$, SmMn$_2$Si$_2$, Mn$_2$Si$_3$, and an unknown phase were obtained, and for the Gd–Mn–Si system, only GdMn$_2$Si$_2$ was obtained, whole crystals of RMnSi (TiNiSi- and PbCl$_2$-type structures) and R$_2$Mn$_2$Si$_3$ (Sc$_2$FeSi$_3$-type structure)\textsuperscript{7} were not detected by XRD. The RMn$_2$Si$_2$ single crystals, having a silver-gray and metallic luster, were generally obtained in the form of thin plates with well-developed (001) faces as shown in Fig. 2 (NdMn$_2$Si$_2$). The largest crystals have maximum dimensions of approximately 2.3 × 2.3 × 0.02 mm$^3$. However, LaMn$_2$Si$_2$ was generally obtained as powder of irregular shape.

The basic crystal data and chemical compositions of RMn$_2$Si$_2$ (R = Ce, Pr, Nd, Sm and Gd) are listed in Table 1. The unit cell parameters of RMn$_2$Si$_2$ crystals are in relatively good agreement with previously published data ($a = 0.4010\pm\text{0.0005}$ nm and $c = 1.0523\pm\text{0.0005}$ nm for CeMn$_2$Si$_2$; $a = 0.4025\pm\text{0.0005}$ nm and $c = 1.0555\pm\text{0.0005}$ nm for PrMn$_2$Si$_2$; $a = 0.4015\pm\text{0.0005}$ nm and $c = 1.0542\pm\text{0.0005}$ nm and $a = 0.4011\pm\text{0.0005}$ nm and $c = 1.0552\pm\text{0.0005}$ nm for NdMn$_2$Si$_2$; $a = 0.3975\pm\text{0.0005}$ nm and $c = 1.0520\pm\text{0.0005}$ nm for SmMn$_2$Si$_2$; $a = 0.3950\pm\text{0.0005}$ nm and $c = 1.0478\pm\text{0.0005}$ nm for GdMn$_2$Si$_2$).\textsuperscript{7} The EDX results show that RMn$_2$Si$_2$ compounds have homogeneity ranges. No evidence has been obtained for the presence of a lead-containing phase in the crystals as concluded from the EPMA and EDX of RMn$_2$Si$_2$ crystals.

The microhardness values of CeMn$_2$Si$_2$, PrMn$_2$Si$_2$, NdMn$_2$Si$_2$, SmMn$_2$Si$_2$ and GdMn$_2$Si$_2$ are 5.8 ± 0.6, 6.5 ± 0.5, 6.3 ± 0.4, 6.5 ± 0.4 and 6.8 ± 0.2 GPa, respectively. The microhardness values of RMn$_2$Si$_2$ (R = Ce, Pr, Nd, Sm and Gd) crystals have not been reported in the earlier literature. These values of RMn$_2$Si$_2$ (R = Ce, Pr, Nd, Sm and Gd) are found to be very similar to previously published data for RMn$_2$Si$_2$ (R = Er, Tb, Yb, Lu and Y) observed in the range of 5.0 ± 0.4 to 7.9 ± 0.3 GPa.\textsuperscript{5, 6}

The oxidation process of RMn$_2$Si$_2$ (R = Ce, Pr, Nd, Sm and Gd) crystals was studied below 1473 K by TG–DTA analyses, as shown in Fig. 3.

![Fig. 2. SEM micrograph of NdMn$_2$Si$_2$ crystal.](image1)

Fig. 1. Powder XRD patterns of the products obtained from R–Mn–Si (R = La, Ce, Pr, Nd, Sm and Gd) systems.

○ RMn$_2$Si$_2$, ○ MnSi, △ Mn$_2$Si$_3$, × unknown.

![Fig. 3. TG–DTA curves of RMn$_2$Si$_2$ (R = Ce, Pr, Nd, Sm and Gd) crystals heated in air.](image2)
Table 1. Results of the Unit Cell Parameters and Chemical Analyses for RMn$_2$Si$_2$ (R = Ce, Pr, Nd, Sm and Gd) Crystals

<table>
<thead>
<tr>
<th>Compound</th>
<th>Crystal</th>
<th>a (nm)</th>
<th>c (nm)</th>
<th>V (nm$^3$)</th>
<th>R (mass%)$^*$</th>
<th>Mn (mass%)$^*$</th>
<th>Si (mass%)$^*$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CeMn$_2$Si$_2$</td>
<td>plate</td>
<td>0.4009(1)</td>
<td>1.0667(1)</td>
<td>0.1691(1)</td>
<td>44.4</td>
<td>37.4</td>
<td>18.2</td>
</tr>
<tr>
<td>PrMn$_2$Si$_2$</td>
<td>plate</td>
<td>0.4029(1)</td>
<td>1.0562(1)</td>
<td>0.1714(1)</td>
<td>47.2</td>
<td>36.3</td>
<td>17.9</td>
</tr>
<tr>
<td>NdMn$_2$Si$_2$</td>
<td>plate</td>
<td>0.4006(1)</td>
<td>1.0542(1)</td>
<td>0.1693(1)</td>
<td>47.8</td>
<td>36.3</td>
<td>18.5</td>
</tr>
<tr>
<td>SmMn$_2$Si$_2$</td>
<td>plate</td>
<td>0.3973(1)</td>
<td>1.0510(1)</td>
<td>0.1659(1)</td>
<td>47.2</td>
<td>35.1</td>
<td>17.7</td>
</tr>
<tr>
<td>GdMn$_2$Si$_2$</td>
<td>plate</td>
<td>0.3947(1)</td>
<td>1.0470(1)</td>
<td>0.1631(1)</td>
<td>47.2</td>
<td>36.3</td>
<td>18.6</td>
</tr>
</tbody>
</table>

$^*$EDX results

Crystal structure: tetragonal, space group 14/mmm, formula units per unit cell Z = 2

Table 2. Results of the TG/DTA Measurements for RMn$_2$Si$_2$ (R = Ce, Pr, Nd, Sm and Gd) Compounds

<table>
<thead>
<tr>
<th>Compound</th>
<th>Oxidation weight gain</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>start (K)</td>
</tr>
<tr>
<td>CeMn$_2$Si$_2$</td>
<td>738</td>
</tr>
<tr>
<td>PrMn$_2$Si$_2$</td>
<td>979</td>
</tr>
<tr>
<td>NdMn$_2$Si$_2$</td>
<td>999</td>
</tr>
<tr>
<td>SmMn$_2$Si$_2$</td>
<td>784</td>
</tr>
<tr>
<td>GdMn$_2$Si$_2$</td>
<td>763</td>
</tr>
</tbody>
</table>

The oxidation of CeMn$_2$Si$_2$, PrMn$_2$Si$_2$, NdMn$_2$Si$_2$, SmMn$_2$Si$_2$ and GdMn$_2$Si$_2$ crystals began to proceed at approximately 738, 979, 999, 784 and 763 K, respectively. The weight gain of the compounds after heating in air up to 1473 K was 29.2, 26.8, 16.4, 19.6 and 23.9 mass%, respectively. CeMn$_2$Si$_2$ had a low oxidation resistance, while NdMn$_2$Si$_2$ had a relatively high oxidation resistance. The final oxidation products were R$_2$Si$_2$O$_7$ (R = Ce, Pr, Nd, Sm and Gd), R$_2$O$_3$ (R = Ce, Sm and Gd), MnSiO$_3$, Mn$_2$Si$_2$, Mn$_2$Si$_2$, and an unknown phase, and so the exothermic peaks are attributed to oxidation products. The results of TG-DTA are listed in Table 2.

Magnetic characterization of the RMn$_2$Si$_2$ (R = Ce, Pr, Nd, Sm and Gd) samples was carried out by measuring the magnetic susceptibilities. Our results agree with recent previous work which has been done on these compounds.9-11

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