The microstructural features of FeCoCrNi, FeCoCrNiAl and FeCoCrNiSi, \( x = 0, 5, 10, 15, 20 \) alloys have been investigated in the present study. The microstructure of FeCoCrNi alloy changes dramatically with equiatomic addition of Al. The fcc irregular shaped grain structure in the as-cast FeCoCrNi alloy changes into the bcc interconnected structure with phase separation of Al-Ni rich and Cr-Fe rich phases in the as-cast FeCoCrNiAl alloy. The microstructure of FeCoCrNi alloy changes with the addition of Si. With increasing the amount of Si, the fcc structure of the grains is maintained, but new phase containing higher amount of Si forms at the grain boundary. As the amount of Si increases, the fraction the Si-rich grain boundary phase increases.

**Key Words:** High entropy alloy, FeCoCrNi alloy, Solid solution, Si addition
MATERIALS AND METHODS

The FeCoCrNi, FeCoCrNiAl, and FeCoCrNiSi\(x=0, 5, 10, 15, 20\) alloy ingots were alloyed from high-purity elements using arc melting in water-cooled molds under argon atmosphere. The ingots were re-melted at least three times to improve their chemical homogeneity. The nominal chemical compositions are listed in Table 1. The alloy ingots were re-melted, and poured into the cylinder-type molds with the diameter of 2 and 5 mm. The microstructure of the specimens were compared after polishing and etching. The specimens were observed under a scanning electron microscope (SEM, JSM-7001F; JEOL, Japan). The chemical composition of the phases in these alloys was analyzed by energy dispersive spectrometry (EDS, S1-ADD0069; Oxford Instruments, UK) assembled in SEM. X-ray diffractometer (XRD, Ultima IV; Rigaku, Japan) with Cu K\(\alpha\) radiation for a 2\(\theta\) range of 30° to 80° at a speed of 4°/min was used for identification of the crystalline structures in the alloys.

Table 1. Chemical compositions of the alloys investigated in the present study (at%)

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Al</th>
<th>Co</th>
<th>Cr</th>
<th>Fe</th>
<th>Ni</th>
<th>Si</th>
</tr>
</thead>
<tbody>
<tr>
<td>CoCrFeNi</td>
<td>-</td>
<td>25</td>
<td>25</td>
<td>25</td>
<td>25</td>
<td>-</td>
</tr>
<tr>
<td>AlCoCrFeNi</td>
<td>20</td>
<td>20</td>
<td>20</td>
<td>20</td>
<td>20</td>
<td>-</td>
</tr>
<tr>
<td>CoCrFeNiSi(_x)</td>
<td>-</td>
<td>23.75</td>
<td>23.75</td>
<td>23.75</td>
<td>23.75</td>
<td>5</td>
</tr>
<tr>
<td>CoCrFeNiSi(_{x=0})</td>
<td>-</td>
<td>22.5</td>
<td>22.5</td>
<td>22.5</td>
<td>22.5</td>
<td>10</td>
</tr>
<tr>
<td>CoCrFeNiSi(_{x=10})</td>
<td>-</td>
<td>21.25</td>
<td>21.25</td>
<td>21.25</td>
<td>21.25</td>
<td>15</td>
</tr>
<tr>
<td>CoCrFeNiSi(_{x=20})</td>
<td>-</td>
<td>20</td>
<td>20</td>
<td>20</td>
<td>20</td>
<td>20</td>
</tr>
</tbody>
</table>

![Fig. 1. X-ray diffractometer patterns obtained from the as-cast FeCoCrNi (A) and FeCoCrNiAl (B) alloys.](image1)

![Fig. 2. Scanning electron microscope images with low (A) and high (B) magnification obtained from the as-cast FeCoCrNi alloy. Energy dispersive spectrometry results obtained from the area marked 'a', 'b', and 'c' in Fig. 2B.](image2)
RESULTS AND DISCUSSION

Effect of Al Addition in FeCoCrNi Alloy

Fig. 1 shows the XRD patterns obtained from the as-cast FeCoCrNi and FeCoCrNiAl alloys (diameter, 2 mm). The diffraction peaks from the as-cast FeCoCrNi alloy were identified as a single fcc phase with the lattice parameter of 0.357 nm, while those form the as-cast FeCoCrNiAl alloy were identified as a single bcc phase with the lattice parameter of 0.287 nm. Fig. 2 shows the low and high magnification SEM images obtained from the as-cast FeCoCrNi alloy together with the EDS results taken from the area marked ‘a’, ‘b’, and ‘c’ in Fig. 2B. From the SEM image in Fig. 2A, the as-cast FeCoCrNi alloy consisted of irregular-shaped grains without any secondary solidification phase. The composition of the grains marked ‘a’, ‘b’, and ‘c’ in Fig. 2B were 26.4% Cr-23.7% Fe-25.7% Co-24.3% Ni, 26.4% Cr-23.2% Fe-25.8% Co-24.6% Ni, and 26.3% Cr-24.4% Fe-23.6% Co-25.7% Ni, respectively (hereafter, the composition is in at%), indicating that the composition is almost homogeneous throughout the whole grains. On the other hand, the as-cast FeCoCrNiAl alloy exhibited a very much different microstructure, as can be seen from the low magnification SEM image in Fig. 3A. The microstructure consisted of a very complicated interconnected structure, indicating that phase separation occurred during solidification. The EDS results obtained from the regions marked ‘a’ and ‘b’ in Fig. 3B show that the compositions after phase separation were 1.76% Al-47.46% Cr-27.5% Fe-17.5% Co-5.82% Ni and 30.94% Al-11.84% Cr-15.1% Fe-19.6% Co-22.49% Ni, respectively. The result indicates that the phase separation occurred into Al-Ni rich and Cr-Fe rich phases. The result in Fig. 1-3 suggest that the
Microstructural Features of High Entropy Alloys

Microstructure of FeCoCrNi alloy changes dramatically with equiatomic addition of Al. In other words, the fcc irregular shaped grain structure with homogeneous composition distribution changes into the bcc interconnected structure with phase separation forming Al-Ni rich and Cr-Fe rich phases.

Effect of Si Addition in FeCoCrNi Alloy
Fig. 4 compares the XRD patterns obtained from the as-cast FeCoCrNiSi(x=0, 5, 10, 15, 20) alloys (diameter, 2 mm). As mentioned above, the as-cast FeCoCrNi alloy consisted of a single solid solution with the fcc structure. With addition of 5% and 10% of Si, the alloy still consisted of the fcc structure, as can be seen from the diffraction peaks in Fig. 4. However, with addition of 15% and 20%, the diffraction peaks from the fcc structure still remained, but new diffraction peaks from the other phase appeared, as can be seen in Fig. 4. Fig. 5A shows the SEM image obtained from the as-cast FeCoCrNiSi5 alloy. The microstructure was almost same as that of alloy without Si shown in Fig. 2. The compositions measured by EDS from the area marked in Fig. 5 are listed in Table 2. The composition of the solid solution was 5.0% Si-24.0% Cr-25.2% Fe-23.7% Co-22.1% Ni, indicating that Si was homogeneously distributed in the grains. When higher amount of Si, 10% was added in the FeCoCrNi alloy, new phase began to form at the grain boundary of the fcc grains, as can be seen in Fig. 5B. The composition measured from the regions from 'a' and 'b' in Fig. 5B were 22.4% Si-19.4% Cr-16.1% Fe-16.2% Co-26.1% Ni and 10.8% Si-24.6% Cr-22.8% Fe-21.5% Co-20.4% Ni, respectively. The result shows that Si was enriched in the phase formed at the grain boundaries. The crystal structure of the Si-rich phase could not be determined in the present study. When the Si content was further increased up to 15%, the fraction of Si-rich phase increased significantly, as can be seen in Fig. 5C. The compositions measured from the regions from 'a' and 'b' in
<table>
<thead>
<tr>
<th>Element</th>
<th>Si</th>
<th>Cr</th>
<th>Fe</th>
<th>Co</th>
<th>Ni</th>
</tr>
</thead>
<tbody>
<tr>
<td>FeCoCrNiSi&lt;sub&gt;a&lt;/sub&gt; Grain</td>
<td>5.0</td>
<td>24.0</td>
<td>25.2</td>
<td>23.7</td>
<td>22.1</td>
</tr>
<tr>
<td>FeCoCrNiSi&lt;sub&gt;b&lt;/sub&gt; a'</td>
<td>24.3</td>
<td>19.5</td>
<td>15.8</td>
<td>17.9</td>
<td>22.5</td>
</tr>
<tr>
<td>FeCoCrNiSi&lt;sub&gt;b&lt;/sub&gt; b'</td>
<td>27.7</td>
<td>8.7</td>
<td>10.3</td>
<td>16.3</td>
<td>37.0</td>
</tr>
<tr>
<td>FeCoCrNiSi&lt;sub&gt;b&lt;/sub&gt;</td>
<td>25.0</td>
<td>17.2</td>
<td>17.3</td>
<td>17.4</td>
<td>23.2</td>
</tr>
</tbody>
</table>

*The results obtained from the area marked in Fig. 5.

Fig. 5C were 24.3% Si-19.5% Cr-15.8% Fe-17.9% Co-22.5% Ni and 13.1% Si-22.4% Cr-23.4% Fe-22.3% Co-18.9% Ni, respectively. The compositions of the Si-rich grain boundary phase and the fcc structure grain were almost same as those in the alloy containing 5% Si. However, it can be noticed that Si-Ni rich phase (27.7% Si-8.7% Cr-10.3% Fe-16.3% Co-37.0% Ni) is newly formed in the Si-rich phase. When Si content was 20%, the microstructure mostly consisted of Si-Ni rich phase. The result in Fig. 4 and 5 indicates that the microstructure of FeCoCrNi alloy changes dramatically with the addition of Si. With increasing the amount of Si, the fcc structure of the grains is maintained, but new phase containing higher amount of Si forms at the grain boundary. As the amount of Si increases, the fraction the Si-rich grain boundary phase increases.

**CONCLUSIONS**

In the study, the microstructural features of FeCoCrNi, FeCoCrNiAl, and FeCoCrNiSi<sub>x</sub> (x=0, 5, 10, 15, 20) alloys have been investigated. The main conclusions are as follows: (1) The microstructure of FeCoCrNi alloy changes dramatically with equiatomic addition of Al. The fcc irregular shaped grain structure with homogeneous composition distribution in the as-cast FeCoCrNi alloy changes into the bcc interconnected structure with phase separation forming Al-Ni rich and Cr-Fe rich phases in the as-cast FeCoCrNiAl alloy. (2) The microstructure of FeCoCrNi alloy changes with the addition of Si. With increasing the amount of Si, the fcc structure of the grains is maintained, but new phase containing higher amount of Si forms at the grain boundary. As the amount of Si increases, the fraction the Si-rich grain boundary phase increases.

**CONFLICT OF INTEREST**

No potential conflict of interest relevant to this article was reported.

**REFERENCES**


