Phase Changes of Zr Added Sm-Fe-V Alloys around the Compound Sm$_5$(Fe,V)$_{29}$

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The effect of Zr additions on phase changes in the Sm-Fe-V system, around the compound Sm$_5$(Fe,V)$_{29}$ was investigated. In Sm$_{4.2-2.9}$V$_8$Zr$_x$ (x=7.7-8.9, y=0-1.6) alloys homogenized at temperatures above 1453K, the hexagonal Th$_2$Ni$_1$-type (2-17H) phase, which was not observed in the ternary alloys, is present as the main phase. However, in the alloys homogenized at temperatures below 1373K, the 2-17H phase is not observed and the Sm$_5$(Fe,V)$_{29}$-type (3-29) and Th$_2$Zn$_1$-type (2-17R) phases are present, accompanied by a small amount of ThMn$_1$-type (1-12) phase, in which α-(Fe,V) is embedded. In Sm$_{4.2}$Fe$_{4.2}$V$_8$Zr$_{1.2}$ alloys homogenized at 1473 K for 20 h, XRD showed that the 2-17H phase transforms into 3-29 and TbCu$_2$-type (1-7) phases after annealing for 4h up to 1323K, and into 3-29 and 2-17R after annealing at 1423K. TEM observations revealed that these grains consist of a submicron scale, two phase mixture. This is the first report of two phase decomposition in the Sm-Fe-V system, however, the coercivities of the nitrided alloys in which the two phase mixture was observed, were small (37 kAm$^{-1}$).

Key words: phase transformation, Th$_2$Ni$_1$, Sm$_5$(Fe,V)$_{29}$, Th$_2$Zn$_1$, ThMn$_1$, nitriding, coercivity

1. Introduction

After the discovery of the Nd$_5$Fe$_{14}$B compound, a range of intermetallic compounds with rare earths (RE) and 3d transition metals were investigated by many researchers. In 1992, Collocott et al. reported the intermetallic compound RE$_7$(Fe,M)$_{29}$ (3-29), which has a monoclinic structure. In common with RE$_7$Fe$_{29}$ compounds, nitriding greatly increases the magnetic properties of the 3-29 compound. Suzuki et al. reported that it may be possible to form a "pinning type" magnet similar to Sm(Co, Fe, Cu, Zr)$_{4.5}$ from nitrided Sm$_5$(Fe,V)$_{29}$ alloy powders. In our previous work, the phase relation of the Sm-Fe-V system was investigated by constructing isothermal sections around the iron rich corner. However, the effect of additional elements on these phase relationships was not clear. Therefore, this study aims to clarify the effect of the addition of Zr on the phase relations in the Sm-Fe-V system.

2. Experimental Procedures

Sm$_{4.2-2.9}$V$_8$Zr$_x$ (x=7.7, 7.8, 8.2, 8.9, y=1.2, 1.6) alloys, with compositions surrounding the Sm$_5$(Fe,V)$_{29}$ (3-29) compound, were induction-melted and cast into a Cu mold in an Ar atmosphere. The cast ingots were heat-treated at 1373-1473K for 20h in an Ar atmosphere, and then quenched in water. Subsequent heat treatments at temperatures between 1223-1423K for 4h, were carried out. In order to investigate the magnetic properties, heat-treated alloy powders were crushed to give a particle size under 63μm, and then nitrided at 813K for 4h. Magnetic properties were measured using a VSM.

Microstructural observations were performed by optical microscopy, SEM-EDX and TEM. The phases present in the ingots were identified by XRD using Fe-Kα radiation.

3. Results and Discussions

Figure 1 shows the XRD patterns of the Sm$_5$(Fe$_{4.2-2.9}$V$_8$Zr$_x$ alloys homogenized at 1453 or 1473K for 20h. All of the alloys had an XRD peak around 29=52°, which is a typical peak for the Th$_2$Ni$_1$-type (2-17H) phase. This suggests that all the alloys contained the 2-17H phase, which was not observed in the ternary alloys in our previous work. The XRD peak of α-(Fe,V) was also observed in all the alloys, however, the intensity of the peak decreased with increasing x, when alloys with same Zr content are compared. From the microstructural observation, the Sm$_5$(Fe$_{4.2}$V$_8$Zr$_{1.2}$ (x=8.9, y=1.2) alloy consisted of almost single phase 2-17H.

Figure 2 shows the XRD patterns of the same alloys homogenized at 1373K for 20h. Typical XRD peaks of the Sm$_5$(Fe,V)$_{29}$ (3-29) phase around 29=50.5° and 47°, and of α-(Fe,V), were observed in all of samples. These alloys also had peaks around 29=48° and 55°, which may be due to either the Th$_2$Zn$_1$-type (2-17R) or the ThMn$_1$-type (1-12) phase. Microstructural observations revealed the presence of 1-12 phase surrounding the α-(Fe,V) in

![Fig. 1 XRD patterns of SmFe$_{4.2-2.9}$V$_8$Zr$_x$ alloys](image-url)
Fig. 2 XRD patterns of Sm$_{1-x}$Fe$_{4.2-2x}$V$_{5.8}$Zr$_x$ alloys homogenized at 1373K for 20h.

Sm$_x$Fe$_{8.2}$V$_{5.8}$Zr$_{1.2}$ (x=7.7, y=1.2) and Sm$_x$Fe$_{8.2}$V$_{5.8}$Zr$_{1.2}$ (x=8.2, y=1.2) alloys. Therefore, it is possible that this 1-12 phase forms from a reaction between α-(Fe, V) and the 3-29 (or 2-17R) matrix phase. The Sm$_x$Fe$_{8.2}$V$_{5.8}$Zr$_{1.2}$ (x=8.9, y=1.2) alloy consisted of the two phases, 3-29 and 2-17R, whereas the alloy with the composition x=7.8 and y=1.6, consisted of 3-29 and 1-12. Table 1 summarizes the phase changes after homogenization. From these results, it is concluded that the 2-17H phase, which is present at temperatures above 1453K, transforms to the 3-29 and 2-17R phases at temperatures lower than 1373K.

A further heat treatment at a lower temperature than 1453K, was carried out in order to bring about further phase transformations. Figure 3 shows XRD patterns of the Sm$_{1-x}$Fe$_{4.2-2x}$V$_{5.8}$Zr$_{1.2}$ (x=8.2, y=1.2) homogenized at 1473K for 20h and subsequently aged at 1223-1423K for 4h.

Fig. 3 XRD patterns of Sm$_{1-x}$Fe$_{4.2-2x}$V$_{5.8}$Zr$_{1.2}$ (x=8.2, y=1.2) homogenized at 1473K for 20h, and then aged at 1223-1423K for 4h.

The aged alloys, the XRD peaks of the 2-17H phase had disappeared, leaving 3-29 phase as the main phase. The alloy aged at 1223K had XRD peaks at around 2θ=48° and 55°, which are typical peaks for the 1-12 and 2-17R phases, however, the peak around 2θ=62°, which is typical of 3-29 and 2-17R phase, was not observed. Therefore, it may be concluded that the phases present in the alloy aged at 1223K are 3-29 and 1-12. In the alloy aged at 1423K, XRD peaks around 2θ=48°, 55° and 62° were observed, which shows that the 3-29 and 2-17R phases were present. The XRD peaks observed in the alloy aged at 1323K, were indexed with the 3-29 phase, however, analysis of the peak intensities suggests that the TbCu$_2$-type (1-7) phase may also be present. This is supported by EDX analysis which showed a deviation from the 3-29 stoichiometric composition.

The corresponding microstructures, observed by optical microscopy, are shown in Fig. 4. It was found that the matrix phase of all the aged alloys was 3-29, and that the 1-12 phase was present surrounding the α-(Fe, V). In the 3-29 matrix phase of the alloy aged at 1323K, a two phase submicron structure was observed by TEM, as shown in Fig. 5. This TEM micrograph shows a lamellae structure, consisting of light and dark phases of about 0.2μm in width. XRD analysis, suggests that these two phases are 3-29 and 1-7. The alloys with other compositions had similar microstructures after homogenization at 1473K for 20h, and subsequent aging at 1323K for 4h. Therefore, it may be said that the two phase microstructure is formed by a phase transformation from the 2-17H phase during aging, and that Zr addition is effective in stabilizing 2-17H and thereby causing this phase transformation. This is the first report of two phase decomposition in the Sm-Fe-V system.

The aging time dependence of the phase transformation

Table 1 Phases present in the homogenized alloys.

<table>
<thead>
<tr>
<th>Sm$<em>{1-x}$Fe$</em>{4.2-2x}$V$_{5.8}$Zr$_x$</th>
<th>1473K (1453K)</th>
<th>1373K</th>
</tr>
</thead>
<tbody>
<tr>
<td>x=7.7, y=1.2</td>
<td>2-17H, α-(Fe, V)</td>
<td>3-29, 2-17R, 1-12, α-(Fe, V)</td>
</tr>
<tr>
<td>x=8.2, y=1.2</td>
<td>2-17H, α-(Fe, V)</td>
<td>3-29, 2-17R, 1-12, α-(Fe, V)</td>
</tr>
<tr>
<td>x=8.9, y=1.2</td>
<td>2-17H</td>
<td>3-29, 2-17R</td>
</tr>
<tr>
<td>x=7.8, y=1.6</td>
<td>2-17H, α-(Fe, V)</td>
<td>3-29, 1-12</td>
</tr>
</tbody>
</table>

Fig. 4 Optical microstructures corresponding to the samples in Fig. 3.

Fig. 5 TEM micrographs of Sm$_2$Fe$_{84.8}$V$_5$Zr$_{1.2}$ homogenized at 1473K for 20h, and then aged at 1323K for 4h.

Fig. 6 Optical micrographs of Sm$_2$Fe$_{84.8}$V$_5$Zr$_{1.2}$ homogenized at 1473K for 20h, and then aged at 1323K for 10-720min.

became coarse and disappeared after aging for 720min. XRD analysis was carried out for the sample annealed for 720min, which revealed that the alloy consisted of 3-29 and 2-17R phases. Therefore, it can be concluded that the aging treatment causes the following phase changes: 2-17H $\rightarrow$ 3-29 + 1-7 $\rightarrow$ 3-29 + 2-17R. However, the alloy with a two phase microstructure only had a small coercivity of 37kAm$^{-1}$ after nitriding. Further studies are needed on additives such as Cu, which helps to increase the difference in wall energy between the phases in Sm-Co 2-17 type magnets, in order to increase the coercivity.

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References