# High-temperature stability of ThMn<sub>12</sub> magnet materials

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# 1. Introduction

We showed that the nitrogenated R = Nd compound  $(Nd_{0.7}Zr_{0.3})(Fe_{0.75}Co_{0.25})_{11.5}Ti_{0.5}N_{1.30}$  had good magnetic properties of  $J_s = 1.67$  T and  $H_a = 5.25$  MA/m at room temperature (RT). The R = Sm alloy,  $(Sm_{0.8}Zr_{0.2})(Fe_{0.75}Co_{0.25})_{11.5}Ti_{0.5}$ , also had  $J_s = 1.58$  T and  $H_a = 5.90$  MA/m at RT. The values in the R = Sm alloy were  $J_s$ = 1.50 T and  $H_a = 3.70$  MA/m at 473 K, and were higher than those of the Nd<sub>2</sub>Fe<sub>14</sub>B phase at this temperature [1]-[3]. Because the R = Sm alloy is a Dy-free and N-free powder, it is a promising candidate for sintered magnets. We investigated the site occupation of Nd, Ti, Zr, and Co in these compounds in the ThMn<sub>12</sub> structure using Cs-corrected scanning transmission electron microscopy [4], [5].

In this study, we studied the high-temperature (700–1300 K) stability of three typical 1-12 compounds, the nitrogenated alloys,  $(Nd_{0.7}Zr_{0.3})(Fe_{0.75}Co_{0.25})_{11.5}Ti_{0.5}N_{1.2}$ ,  $Nd(Fe_{0.8}Co_{0.2})_{11}Mo_{1.0}N_{1.0}$ , and the non-nitrogenated alloy,  $(Sm_{0.8}Zr_{0.2})(Fe_{0.75}Co_{0.25})_{11.5}Ti_{0.5}$ . The two nitrogenated compounds were selected because of their high magnetic properties ( $-Ti_{0.5}N_{1.2}$ ) and stability at high temperatures of up to 900 K ( $-Mo_{1.0}N_{1.0}$ ). The third R = Sm alloy was selected for its high magnetic properties at high temperatures [3], and the likelihood that it could be sintered around 1300 K.

In the presentation, we will report about the high temperature stability of above three compounds, but we concentrate our discussion to  $(Sm_{0.8}Zr_{0.2})(Fe_{0.75}Co_{0.25})_{11.5}Ti_{0.5}$  compound in this manuscript due to the limitation of space.

#### 2. Experimental and Results

XRD at RT was performed under the following conditions: CuK $\alpha$ :  $\lambda = 0.1542$  nm; scanning speed,  $2\theta = 5^{\circ}$ /min; sampling, each  $\theta = 0.1^{\circ}$ ; atmosphere, Ar ( $Po_2 \approx 10^{-2}$  Pa). The penetration depth of the X-rays (Cu K $\alpha$ ) was estimated to be about 2 µm (similar to the case of  $\alpha$ -Fe). The samples were heated at a rate of 10 K/min to each treatment temperature and held at the temperature for 1 h and cooling down, before the XRD measurements at RT. The XRD patterns of the treated samples were indicated in Figure.

We examined the effect of oxidation, which causes the decomposition of  $(Sm_{0.8}Zr_{0.2})(Fe_{0.75}Co_{0.25})_{11.5}Ti_{0.5}$  compound (appearance of the  $\alpha$ -(Fe, Co) phase), on the stability of the 1-12 phase. The sample was heated at 1073 K in Ar ( $Po_2 = 10^{-2}$  Pa) and in Ar with oxygen removing by using a ZrO<sub>2</sub> ceramic oxygen pump ( $Po_2 = 10^{-15}$  Pa; low  $PO_2$ ) (in figure; 1073K 1h and 1073K 1h low- $Po_2$ , respectively). The temperature increased to 1273 K in the atmosphere also with oxygen removing ( $Po_2 = 10^{-15}$  Pa; low  $Po_2$ ) (also in figure; 1273K 1h low  $Po_2$ ). The



Figure. XRD patterns observed for  $((Sm_{0.8}Zr_{0.2}) - (Fe_{0.75}Co_{0.25})_{11.5}Ti_{0.5})$ . The atmosphere during heat treatment was controlled and measured by using a ZrO<sub>2</sub> ceramic oxygen pump and sensor.

intensities of the strongest peak of the  $\alpha$ -(Fe, Co) phase at about  $2\theta = 44.5^{\circ}$  with CuK $\alpha$  diffraction are similar in all treatments as shown in the figure. Therefore, the oxidation was not the main reason for the decomposition of this compound, but heat treatment at >873 K decreased the phase stability.

### 3. Discussion

From other XRD studies using a high temperature XRD, it was revealed that the  $(Sm_{0.8}Zr_{0.2})(Fe_{0.75}Co_{0.25})_{11.5}Ti_{0.5}$  compound decomposed readily in a high *PO*<sub>2</sub> atmosphere, i.e disappearing of the XRD diffraction peaks of 1-12 phase, that is in the *PO*<sub>2</sub> was estimated to be >10 Pa [6]. In contrast, the 1-12 structure was stable up to 1273 K at a low *PO*<sub>2</sub> of  $10^{-15}$  Pa in an Ar atmosphere where oxygen was eliminated by using a ZrO<sub>2</sub> oxygen pump as shown in Figure of this manuscript. Therefore, the oxidation is an important reason of decomposition of the  $(Sm_{0.8}Zr_{0.2})(Fe_{0.75}Co_{0.25})_{11.5}Ti_{0.5}$  compound.

Another important characteristic of 1-12 compounds is that the ThMn<sub>12</sub> structure is stable at high temperatures approximately above 1100 K. Therefore, the ThMn<sub>12</sub> structure observed by using XRD at RT was a metastable phase. If we heated the structure for several hours at 800–900 K, the structure gradually decomposed into other phases [7]. A characteristic phase appearing after decomposition is the  $\alpha$ -Fe phase. When the (Sm<sub>0.8</sub>Zr<sub>0.2</sub>)(Fe<sub>0.75</sub>Co<sub>0.25</sub>)<sub>11.5</sub>Ti<sub>0.5</sub> compound was heated in a high *PO*<sub>2</sub> atmosphere, the decomposition was accelerated, although the ThMn<sub>12</sub> structure was stable up to 1273 K in a low *PO*<sub>2</sub> of ~10<sup>-15</sup> Pa as shown in Figure of this manuscript, despite the gradual increase of the (110) peak of the  $\alpha$ -Fe phase.

# 4. Conclusion

The ThMn<sub>12</sub> phase was metastable at RT, and the samples decomposed at 800–900 K when the samples were kept for long duration, i.e. for several hours. In the case of  $(Sm_{0.8}Zr_{0.2})(Fe_{0.75}Co_{0.25})_{11.5}Ti_{0.5}$  compound, the decomposition of the main 1-12 phase was accelerated by the oxidation that occurred under a high *PO*<sub>2</sub> atmosphere as *PO*<sub>2</sub>> 10 Pa. Conversely, the main phase was stable up to, and should be more than, 1273 K in a low *PO*<sub>2</sub> of ~10<sup>-15</sup> Pa.

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