Structure and magnetic hysteresis properties of rapidly quenched Nd$_{1-x}$Ce$_x$(Fe$_{0.75}$Co$_{0.25}$)$_{11}$Ti ($x = 0$-0.3) based alloys after annealing

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Abstract. We have studied the effect of the arc-melting, melt-spinning, annealing and doping with cerium on the structure and magnetic hysteresis properties at room temperature of alloys based on the compound Nd(Fe$_{0.75}$Co$_{0.25}$)$_{11}$Ti with the ThMn$_{12}$-type. We found that the optimal combination of magnetic hysteresis properties were obtained for alloys (Nd$_{1-x}$Ce$_x$)Fe$_{11}$Ti at $x = 0.2$ and 0.3 after melt-spinning and annealing.

1. Introduction

The alloys based on intermetallic compounds NdFe$_{12-x-y}$Co$_x$M$_y$N (M = Ti, V, Mo) with ThMn$_{12}$-type refer to promising permanent magnetic materials with high values of saturation magnetization, Curie temperature, magnetic anisotropy field and magnetocrystalline uniaxial anisotropy constant [1-6]. The microstructure of these alloys after melt-spinning or mechanoactivation is the nanostructured state that allows obtaining relatively high coercive force values [7-13]. As seen in [14], relative high values of the magnetic properties at room temperature were obtained for the rapidly quenched alloys (Nd, Ce)(Fe, Mo)$_{12}$ after nitriding (nitrogenation): $T_C = 337$ °C, $H_C = 2.9$ kOe, $(B\cdot H)_{\text{max}} = 1.6$ MG-Oe. Therefore, the study of structural transformations and magnetic properties of the (Nd$_{1-x}$Ce$_x$)(Fe$_{0.75}$Co$_{0.25}$)$_{11}$Ti alloys after melt-spinning followed by annealing is an urgent issue.

2. Experimental

Alloys of the compositions (Nd$_{1-x}$Ce$_x$)(Fe$_{0.75}$Co$_{0.25}$)$_{11}$Ti ($x = 0$-0.3) with a mass 120 g were obtained by arc-melting in an argon gas atmosphere. Rapidly quenched ribbons were obtained from these ingots by melt-spinning with a rotating copper wheel of a DVX-II equipment in an argon gas atmosphere. The linear rotation speed of the copper wheel was 30 m/s. Part of these ribbons was annealed in vacuum at 700 °C for 30 min ribbons and was pulverized to a diameter smaller than 45 µm. The chemical compositions of samples were defined by a X-ray fluorescence wave-dispersion spectrometer Rigaku ZSX Primus II. X-ray diffraction studies were defined by a Rigaku Ultima IV diffractometer (CoK$_{\alpha}$).
radiation, $\lambda = 1.79021$ Å). Spectra were processed by the Rietveld method via the Rigaku PDXL 2 software. Quantity of amorphous phase was defined by the method of Savchenko et al. [15]. The microstructure of the cast alloys were studied by a Tescan Vega 3SB SEM with an Oxford Instruments EDX detector for elemental microanalysis. The microstructure of the quenched samples was studied by a TEM JEOL JEM 1400. The magnetic hysteresis properties of samples were performed using a VSM-250 system in a magnetic field up to 1.6 MA/m (20 kOe) at room temperature.

3. Results and discussion
3.1. Arc-melted alloys
Table 1 shows chemical compositions of the as-cast samples which is very close to nominal compounds Nd$_{1-x}$Ce$_x$(Fe$_{0.75}$Co$_{0.25}$)$_1$Ti with $x = 0, 0.1, 0.2$ and 0.3, respectively. The results of phase analysis are shown in Table 2. Samples after arc-melting were characterized a multi-phase state: (Nd, Ce)(Fe, Co)$_{11}$Ti ($I4/mmm$) (75-86 %), $\alpha$-(Fe, Co) ($Im-3m$) (5-12 %), $\alpha$-(Ti, Fe) ($P6_3/mmc$) (2-5 %), (Nd, Ce)(Fe, Co)$_2$ ($Fd-3m$) (4-8 %) and (Nd, Ce)$_2$(Fe, Co)$_1$ ($R-3m$) (0-8 %). As seen in Table 2, the lattice parameter $a$ of the main phase decreases from 8.569 Å to 8.555 Å as well as lattice parameter $c$ from 4.776 Å to 4.771 Å with increasing Ce content from $x = 0$ to 0.3.

Table 1. Chemical compositions of Nd$_{1-x}$Ce$_x$(Fe$_{0.75}$Co$_{0.25}$)$_1$Ti alloys with $x = 0$-0.3 after arc-melting.

| Sample                | Chemical composition (mass. %) | Total content of impurity elements (mass. %) |
|-----------------------|--------------------------------|--------------------------------------------|
| Nd(Fe$_{0.75}$Co$_{0.25}$)$_1$Ti | 17.70  56.54  19.89  5.87 | -                                          |
| Experiment            | 18.94  53.92  20.01  6.62 | $\leq 0.51$                                |
| Nd$_{0.9}$Ce$_{0.1}$(Fe$_{0.75}$Co$_{0.25}$)$_1$Ti | 15.94  1.81  56.57  19.80  5.88 | -                                          |
| Experiment            | 17.12  2.56  53.21  20.22  6.38 | $\leq 0.51$                                |
| Nd$_{0.8}$Ce$_{0.2}$(Fe$_{0.75}$Co$_{0.25}$)$_1$Ti | 14.17  3.44  56.60  19.91  5.88 | -                                          |
| Experiment            | 15.51  3.43  53.02  20.13  7.45 | $\leq 0.46$                                |
| Nd$_{0.7}$Ce$_{0.3}$(Fe$_{0.75}$Co$_{0.25}$)$_1$Ti | 12.41  5.17  56.63  19.92  5.88 | -                                          |
| Experiment            | 13.15  5.69  54.53  19.26  6.71 | $\leq 0.56$                                |
|                        | $\pm 0.06$  $\pm 0.05$  $\pm 0.03$  $\pm 0.02$  $\pm 0.02$ | -                                          |

The quantitative XRD estimates for the phases observed on the Ce side of the alloy series in cast state are confirmed by the SEM-EDS data. Four phases for $x = 0$ and five phases for others samples are found on the backscattered electrons SEM micrographs of the microstructure (Fig. 1). The chemical composition of the main phase was found to be Nd(Fe$_{0.75}$Co$_{0.25}$)$_1$Ti$_{1.05}$ for $x = 0$, Nd$_{0.85}$Ce$_{0.11}$(Fe$_{0.73}$Co$_{0.27}$)$_{10.71}$Ti$_{1.06}$ for $x = 0.1$, Nd$_{0.75}$Ce$_{0.25}$(Fe$_{0.73}$Co$_{0.27}$)$_{10.33}$Ti$_{1.19}$ for $x = 0.2$ and Nd$_{0.65}$Ce$_{0.35}$(Fe$_{0.73}$Co$_{0.27}$)$_{10.44}$Ti$_{1.22}$ for $x = 0.3$ from the EDS analysis on SEM.
Table 2. The XRD results of the Nd$_{1-x}$Ce$_x$(Fe$_{0.75}$Co$_{0.25}$)$_{11}$Ti alloys in the cast state.

| Sample | Phase composition (Space group) | Content (vol. %) | Lattice parameters | The volume of a unit cell (V, Å$^3$) |
|--------|----------------------------------|------------------|--------------------|------------------------------------|
|        |                                  |                  | $a$, Å  | $c$, Å  | $c/a$   |                                      |
| $x = 0$ | Nd(Fe, Co)$_{11}$Ti (I4/mmm)     | 80.0(8)          | 8.569(9) | 4.776(5) | 0.558   | 350.69(71)                             |
|        | $\alpha$-(Fe, Co) (Im-3m)        | 10.0(4)          | 2.873(7) | 2.873(7) | 1       | 23.72(17)                              |
|        | $\alpha$-(Ti, Fe) (P6/mmc)       | 3.0(4)           | 2.767(4) | 4.216(9) | 1.524   | 27.96(82)                              |
|        | Nd(Fe, Ce)$_2$ (F6-3m)           | 7.0(3)           | 7.332(5) | 7.332(5) | 1       | 394.16(41)                             |
|        | (Nd, Ce)(Fe, Co)$_{11}$Ti (I4/mmm) | 75.0(9)       | 8.560(6) | 4.773(3) | 0.558   | 349.73(41)                             |
|        | $\alpha$-(Fe, Co)                | 8.0(8)           | 2.881(3) | 2.881(3) | 1       | 23.92(42)                              |
| $x = 0.1$ | $\alpha$-(Ti, Fe)             | 3.0(7)           | 2.783(6) | 5.050(7) | 1.814   | 33.88(11)                              |
|        | (Nd, Ce)(Fe, Co)$_2$ (F6-3m)      | 6.0(8)           | 7.313(2) | 7.313(2) | 1       | 391.10(15)                             |
|        | (Nd, Ce)$_2$(Fe, Co)$_7$ (R-3m)    | 8.0(7)           | 8.392(2) | 15.821(7) | 1.885 | 965.01(51)                             |
|        | (Nd, Ce)(Fe, Co)$_{11}$Ti       | 86.0(4)          | 8.559(6) | 4.772(4) | 0.558   | 349.58(41)                             |
|        | $\alpha$-(Fe, Co)                | 5.0(2)           | 2.881(6) | 2.881(6) | 1       | 23.92(91)                              |
| $x = 0.2$ | $\alpha$-(Ti, Fe)              | 2.0(4)           | 2.928(4) | 4.686(6) | 1.600   | 34.79(71)                              |
|        | (Nd, Ce)(Fe, Co)$_2$             | 7.0(9)           | 7.298(2) | 7.298(2) | 1       | 388.70(22)                             |
|        | (Nd, Ce)(Fe, Co)$_{11}$Ti       | 75.0(7)          | 8.555(4) | 4.771(3) | 0.558   | 349.18(31)                             |
| $x = 0.3$ | $\alpha$-(Fe, Co)              | 12.0(2)          | 2.880(9) | 2.880(9) | 1       | 23.88(15)                              |
|        | $\alpha$-(Ti, Fe)                | 5.0(1)           | 2.350(2) | 3.748(4) | 1.595   | 17.92(21)                              |
|        | (Nd, Ce)(Fe, Co)$_2$             | 8.0(6)           | 7.286(5) | 7.286(5) | 1       | 386.80(51)                             |
Figure 1. Backscattered electrons SEM micrographs of Nd$_{1-x}$Ce$_x$(Fe$_{0.75}$Co$_{0.25}$)$_{11}$Ti arc-melted alloys for (a) $x = 0$, (b) $x = 0.1$, (c) $x = 0.2$ and (d) $x = 0.3$.

3.2. Melt-spun and annealed alloys

Results of the XRD analysis for samples after melt-spinning and after annealing at 700 °C for 30 min are shown in Table 3. The volume fraction of compound with the ThMn$_{12}$-type structure after melt-spinning decreases from 93 % to 60 % with increasing a content of Ce from $x = 0$ to 0.3, respectively. The results of X-ray diffraction analysis show that during melt-spinning formation of an amorphous phase is possible. The volume fraction of an amorphous phase increases from 0 % to 32 % with increasing a content of Ce. It was found that melt-spinning leads to the formation of a few content of α-(Fe, Co) phase. The volume of a unit cell of the 1:12 phase for the as-spun samples does non-monotonically change with increasing Ce content due to the presence of an amorphous phase.

Figure 3 shows bright-field TEM image and electron diffraction pattern for the Nd(Fe$_{0.75}$Co$_{0.25}$)$_{11}$Ti as-spun alloy. The TEM analysis is in accordance with the XRD results. The general microstructure of the alloy is the 1:12 phase in an equiaxed polycrystalline state with an average grain size of 100-150 nm. An amorphous phase along the grain boundaries of the main phase for this alloy was not found.

As seen in table 3, the lattice parameter $a$ of the main phase for annealed samples decreases from 8.496 Å to 8.477 Å as well as lattice parameter $c$ from 4.907 Å to 4.875 Å with increasing Ce content from $x = 0$ to 0.3. The maximum volume fraction of the 1:12 phase was obtained for annealed sample with $x = 0.2$. The minimum trace amounts of a bcc α-(Fe, Co) phase with the lattice parameter $a = 2.873$ Å and (Nd, Ce)$_2$O$_3$ phase (P321) with $a = 4.162$ Å and $c = 5.595$ Å were observed in the XRD results. For example, fig. 2 shows diffraction patterns of the Nd$_{0.8}$Ce$_{0.2}$(Fe$_{0.75}$Co$_{0.25}$)$_{11}$Ti sample after arc-melting, melt-spinning and after annealing at 700 °C for 30 min.
Table 3. The XRD results of the Nd<sub>1-x</sub>Ce<sub>x</sub>(Fe<sub>0.75</sub>Co<sub>0.25</sub>)<sub>11</sub>Ti alloys after melt spinning and annealing.

| Sample | Phase composition (Space group) | Content (vol. %) | Lattice parameters | The volume of a unit cell (V, Å<sup>3</sup>) |
|--------|---------------------------------|-----------------|--------------------|---------------------------------------------|
|        |                                 |                 | a, Å               | c, Å                              | c/a |                                |
|        | melt-spinning state              |                 |                    |                                |     |                                |
| x = 0  | Nd(Fe, Co)<sub>11</sub>Ti       | 93.0(8)         | 8.525(2)           | 4.799(2)                         | 0.563 | 348.77(18) |
|        | α-(Fe, Co)                      | 7.0(5)          | 2.872(9)           | 2.872(9)                         | 1    | 23.69(13)  |
| x = 0.1| (Nd, Ce)(Fe, Co)<sub>11</sub>Ti| 71.0(5)         | 8.486(4)           | 4.881(8)                         | 0.575 | 351.50(61) |
|        | α-(Fe, Co)                      | 5.0(1)          | 2.892(3)           | 2.892(3)                         | 1    | 24.18(52)  |
|        | Amorphous                       | 24(3)           | -                 | -                               | -    | -            |
| x = 0.2| (Nd, Ce)(Fe, Co)<sub>11</sub>Ti| 65.0(7)         | 8.506(4)           | 4.808(3)                         | 0.565 | 347.87(33) |
|        | α-(Fe, Co)                      | 9.0(8)          | 2.958(4)           | 2.958(4)                         | 1    | 25.88(62)  |
|        | Amorphous                       | 26(5)           | -                 | -                               | -    | -            |
| x = 0.3| (Nd, Ce)(Fe, Co)<sub>11</sub>Ti| 60.0(4)         | 8.511(4)           | 4.886(4)                         | 0.574 | 353.93(31) |
|        | α-(Fe, Co)                      | 8.0(9)          | 2.900(3)           | 2.900(3)                         | 1    | 24.39(4)   |
|        | Amorphous                       | 32(5)           | -                 | -                               | -    | -            |
|        | annealing state                 |                 |                    |                                |     |                                |
| x = 0.1| (Nd, Ce)(Fe, Co)<sub>11</sub>Ti| 69.0(4)         | 8.496(2)           | 4.907(3)                         | 0.578 | 354.23(14) |
|        | α-(Fe, Co)                      | 15.0(7)         | 2.881(7)           | 2.881(7)                         | 1    | 23.895(11) |
|        | (Nd, Ce)<sub>2</sub>O<sub>3</sub>(P321) | 16.0(6)     | 3.883(5)           | 6.067(7)                         | 1.562 | 65.48(16)  |
| x = 0.2| (Nd, Ce)(Fe, Co)<sub>11</sub>Ti| 87.0(5)         | 8.489(2)           | 4.877(2)                         | 0.575 | 351.45(25) |
|        | α-(Fe, Co)                      | 8.0(3)          | 2.873(4)           | 2.873(4)                         | 1    | 23.73(67)  |
|        | (Nd, Ce)<sub>2</sub>O<sub>3</sub> | 5.0(4)        | 4.162(5)           | 5.595(5)                         | 1.344 | 83.92(16)  |
| x = 0.3| (Nd, Ce)(Fe, Co)<sub>11</sub>Ti| 73.0(5)         | 8.474(3)           | 4.875(3)                         | 0.575 | 350.07(33) |
|        | α-(Fe, Co)                      | 17.0(3)         | 2.872(6)           | 2.872(6)                         | 1    | 23.69(91)  |
|        | (Nd, Ce)<sub>2</sub>O<sub>3</sub> | 10.0(8)       | 3.587(4)           | 5.877(9)                         | 1.638 | 65.48(16)  |
3.3. Magnetic hysteresis properties

Magnetic hysteresis properties for the Nd<sub>1-x</sub>Ce<sub>x</sub>(Fe<sub>0.75</sub>Co<sub>0.25</sub>)<sub>11</sub>Ti alloys in various states are shown in Table 4. The arc-melted alloys were a large-grain state and had low coercive force, $H_c$ (7.9-9.0 kA/m) and remanence magnetization, $\sigma_r$ (3.1-3.5 A·m<sup>2</sup>/kg). Saturation magnetization, $\sigma_s$, decreases from 143 to 138 A·m<sup>2</sup>/kg with increasing a content of Ce from $x = 0$ to 0.3.

Coercive force, remanence magnetization and saturation magnetization only for the Nd(Fe<sub>0.75</sub>Co<sub>0.25</sub>)<sub>11</sub>Ti compound after melt-spinning monotonically increase from 9.0 to 26.5 kA/m, from 3.2 to 17.0 A·m<sup>2</sup>/kg and from 143 to 149 A·m<sup>2</sup>/kg, respectively. This result presumably links with that the 1:12 phase have the nanocrystalline grains which are magnetically coupled with each
other or with a trace amount of some α-(Fe, Co) grains. As seen in Table 4, saturation magnetization for others rapidly quenched alloys monotonically decrease with increasing a content of Ce. Coercive force and remanence magnetization of these samples practically do not change compared with alloys in the cast state presumably because of the presence of an amorphous phase.

As seen in Table 4, coercive force and remanence magnetization of the samples with a content Ce in the range \( x = 0.1 - 0.3 \) increase to 38.3 - 43.1 kA/m and 28.1 - 33.2 A·m²/kg compared with alloys after melt-spinning, respectively. Saturation magnetization of these samples increases from 130 to 137 A·m²/kg with increasing a content Ce in the range 0.1 - 0.3.

Table 4. Magnetic hysteresis properties at room temperature of the \( \text{Nd}_{1-x}\text{Ce}_x(\text{Fe}_{0.75}\text{Co}_{0.25})_1\text{Ti} \) alloys in various states.

| Sample  | Coercive force \( (H_c, \text{kA/m (Oe)}) \) | Remanence magnetization \( (\sigma_r, \text{A}·\text{m}^2/\text{kg}) \) | Saturation magnetization \( (\sigma_s, \text{A}·\text{m}^2/\text{kg}) \) |
|---------|---------------------------------|---------------------------------|---------------------------------|
| arc-melting state |
| \( x = 0 \) | 9.0 (114) | 3.2 | 143 |
| \( x = 0.1 \) | 8.0 (100) | 3.4 | 141 |
| \( x = 0.2 \) | 7.9 (99) | 3.1 | 138 |
| \( x = 0.3 \) | 8.1 (102) | 3.5 | 134 |
| melt-spinning state |
| \( x = 0 \) | 26.5 (334) | 17.0 | 149 |
| \( x = 0.1 \) | 8.2 (103) | 5.3 | 143 |
| \( x = 0.2 \) | 11.6 (146) | 7.8 | 139 |
| \( x = 0.3 \) | 8.3 (104) | 6.0 | 127 |
| annealing state |
| \( x = 0.1 \) | 38.3 (482) | 33.2 | 130 |
| \( x = 0.2 \) | 43.1 (542) | 28.1 | 135 |
| \( x = 0.3 \) | 38.3 (481) | 32.0 | 137 |

The observed differences in the magnetic hysteresis characteristics of the alloys in various states are associated with their features of the microstructure (the volume fractions of constituent phases and their chemical compositions) and substructure (dispersity and a microdeformation).

4. Conclusion
We have obtained magnetic material from the \( \text{Nd}_{1-x}\text{Ce}_x(\text{Fe}_{0.75}\text{Co}_{0.25})_1\text{Ti} \) \( (x = 0-0.3) \) alloys by arc-melting, melt-spinning and annealing. The volume fraction of compound with the ThMn\(_{12}\)-type structure after melt-spinning decreases from 93 % to 60 % with increasing a content of Ce from \( x = 0 \) to 0.3, respectively. The maximum volume fractions of the 1:12 phase were obtained for the as-spun sample with \( x = 0 \) and annealed sample with \( x = 0.2 \). Sample in an almost single-phase state (93 % of 1:12 phase) was produced by melt-spinning with the average grain size about 120 nm. The optimal magnetic hysteresis properties were obtained by a combination of melt-spinning and annealing for \( x = 0.2 \) and \( x = 0.3 \): \( H_c = 43.1 \) and 38.3 kA/m, \( \sigma_r = 28.1 \) and 32 A·m²/kg, \( \sigma_s = 135 \) and 137 A·m²/kg.

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5. References

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