Magnetic hysteresis properties and structure of melt-spun \((\text{Nd}_{0.8-x}\text{Ce}_x\text{Zr}_{0.2})(\text{Fe}_{0.75}\text{Co}_{0.25})_{11.3}\text{Ti}_{0.35}\text{V}_{0.35}\) alloys \((x = 0-0.3)\) after annealing and nitriding

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Abstract. We have studied the effect of the arc-melting, melt-spinning, annealing, nitriding and doping with cerium on the structure and magnetic hysteresis properties at room temperature of alloys based on the compound \((\text{Nd}_{0.8}\text{Zr}_{0.2})(\text{Fe}_{0.75}\text{Co}_{0.25})_{11.3}\text{Ti}_{0.35}\text{V}_{0.35}\) with the ThMn\(_{12}\)-type. We found that the optimal magnetic hysteresis properties were obtained for \((\text{Nd}_{0.8}\text{Ce}_x\text{Zr}_{0.2})(\text{Fe}_{0.75}\text{Co}_{0.25})_{11.3}\text{Ti}_{0.35}\text{V}_{0.35}\) after combined treatment that consists in melt-spinning, annealing, and nitriding.

1. Introduction

The alloys based on intermetallic compounds \(\text{NdFe}_{12-x-y}\text{Co}_x\text{M}_y\text{N}\) \((\text{M} = \text{Ti}, \text{V}, \text{Mo})\) 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 [1-4]. The microstructure of these alloys after melt-spinning or mechanoactivation is the nanostructured state that allows one to reach relatively high coercive force values [5-11]. According to [12], relative high magnetic properties at room temperature were obtained for the rapidly quenched alloys \((\text{Nd}, \text{Ce})(\text{Fe}, \text{Mo})_{12}\) after nitriding: \(T_C = 337 °C, I_H = 2.9 \text{kOe}, (B\cdot H)_{\text{max}} = 1.6 \text{MG\cdot Oe}\). Therefore, the study of structural transformations and magnetic properties of the \((\text{Nd}_{0.8-x}\text{Ce}_x\text{Zr}_{0.2})(\text{Fe}_{0.75}\text{Co}_{0.25})_{11.3}\text{Ti}_{0.35}\text{V}_{0.35}\) alloys after melt-spinning followed by annealing and nitriding is an urgent issue.

2. Experimental

Alloys of the compositions \((\text{Nd}_{0.8-x}\text{Ce}_x\text{Zr}_{0.2})(\text{Fe}_{0.75}\text{Co}_{0.25})_{11.3}\text{Ti}_{0.35}\text{V}_{0.35}\) \((x = 0-0.3)\) 110-120 g in weight were obtained by arc-melting in an argon atmosphere. Rapidly quenched ribbons were obtained from these ingots by melt-spinning in an argon atmosphere using a DVX-II set up equipped with a rotating copper wheel. The linear rotation speed of the copper wheel was 30 m/s. A portion of these ribbons was annealed in vacuum at 700 °C for 15 min and was pulverized into particles less than 45 µm in diameter. The chemical compositions of samples were determined by X-ray fluorescent analysis using a Rigaku ZSX Primus II X-ray fluorescence wave-dispersion spectrometer. X-ray diffraction (XRD) studies were performed on a Rigaku Ultima IV diffractometer \((\text{CoK}_\alpha \text{radiation}, \lambda = 1.79021 \text{Å})\). X ray diffraction patterns were processed by the Rietveld method using the Rigaku PDXL 2 software. The microstructure of the cast alloys was studied on a Tescan Vega 3SB scanning electron microscope (SEM) equipped with an Oxford Instruments EDX detector for elemental microanalysis. The micro-
structure of the rapidly quenched samples was studied by transmission electron microscopy (TEM) using a JEOL JEM 1400 electron microscope. The magnetic hysteresis properties of samples were measured at room temperature in magnetic fields up to 1.6 MA/m (20 kOe) using a VSM-250 system.

3. Results and discussion
3.1. Arc-melted alloys
Table 1 shows chemical compositions of the as-cast samples, which are very close to the (Nd0.8-xCe0.2)(Fe0.75Co0.25)11.3Ti0.35V0.35 nominal compositions with x = 0, 0.1, 0.2, and 0.3. The results of phase analysis are shown in Table 2. Samples after arc-melting were multi-phase: (Nd, Ce, Zr)(Fe, Co, Ti, V)12 (I4/mmm) (65-72 %), α-(Fe, Co) (lm-3m) (20-27 %), (Fe, Co)(Ti, V) (P6/mmm) (0-5 %) and (Nd, Ce)2(Fe, Co)17 (R-3m) (5-10 %). As seen from Table 2, as the Ce content increases from x = 0 to 0.3, the lattice parameter a of the main 1-12 phase decreases from 8.456 Å to 8.413 Å and the lattice parameter c decreases from 4.894 Å to 4.879 Å.

| Table 1. Chemical compositions of as-cast (Nd0.8-xCe0.2)(Fe0.75Co0.25)11.3Ti0.35V0.35 alloys with x = 0-0.3. |
| Sample | Nd | Ce | Zr | Fe | Co | Ti | V | Total content of impurity elements (mass. %) |
|--------|----|----|----|----|----|----|---|------------------------------------------|
| x = 0.0 |    |    |    |    |    |    |   | -                                        |
| Experiment | 14.25±0.05 | 0.00 | 2.26 | 58.58 | 20.60 | 2.07 | 2.21 | ≤ 0.35                                  |
| x = 0.1 | 12.50±0.04 | 3.22 | 2.14 | 58.30 | 20.40 | 2.06 | 2.19 | ≤ 0.49                                  |
| Experiment | 11.00±0.05 | 3.77 | 2.14 | 57.80 | 20.40 | 2.06 | 2.10 | ≤ 0.63                                  |
| x = 0.2 | 8.94±0.06 | 5.13 | 2.18 | 58.70 | 20.50 | 2.10 | 2.10 | ≤ 0.66                                  |
| Experiment | 8.63±0.05 | 5.13 | 2.18 | 58.70 | 20.50 | 2.10 | 2.10 | -                                       |

The results of quantitative XRD analysis of phases observed for the Ce side of the alloy series in cast state are confirmed by the SEM-EDS data. SEM micrographs taken in backscattered electron mode demonstrate the presence of three phases in the sample with x = 0.0 and four phases in other samples (Fig. 1). According to data of SEM-EDS analysis, the chemical composition of the main 1-12 phase was found to be (Nd0.80Zr0.20)(Fe0.74Co0.26)9.8Ti0.23V0.20 for x = 0, (Nd0.74Ce0.11Zr0.21)(Fe0.74Co0.27)9.42Ti0.25V0.20 for x = 0.1, (Nd0.65Ce0.10Zr0.20)(Fe0.73Co0.27)9.49Ti0.27V0.19 for x = 0.2 and (Nd0.68Ce0.07Zr0.22)(Fe0.72Co0.23)9.30Ti0.35V0.22 for x = 0.3.
3.2. Melt-spun, annealed and nitrided alloys

Results of the XRD analysis for samples after melt-spinning and after annealing at 700 °C for 15 min and nitriding are shown in Table 3. The volume fraction of the compound with the ThMn12-type structure after melt-spinning increases non-monotonically from 84 % to 88 % with increasing Ce content from \( x = 0 \) to 0.3. The maximum volume fraction of the 1:12 phase (93 %) was obtained for the sample with \( x = 0.2 \). It was found that the melt-spinning leads to the formation of a small content of \( \alpha- \) (Fe, Co) phase. The unit cell volume \( (V) \) of the 1:12 phase in the as-spun samples also increases non-monotonically with increasing Ce content. The maximum value of \( V = 350.02 \text{ Å}^3 \) was obtained for sample with \( x = 0.2 \).

Fig. 3 shows a bright-field TEM image and electron diffraction pattern for the \((\text{Nd}_{0.8-x}	ext{Ce}_x\text{Zr}_{0.2})(\text{Fe}_{0.75}\text{Co}_{0.25})_{11.3}\text{Ti}_{0.35}\text{V}_{0.35}\) as-spun alloy. The results of TEM analysis agree with the XRD data. The general microstructure of the alloy is the 1:12 phase in an equiaxed polycrystalline state with an average grain size of 120-180 nm. An amorphous phase was found to be present along grain boundaries of the main phase.

As seen from Table 3, the unit cell volume of the main 1:12 phase in annealed samples non-monotonically increases from 344.08 Å\(^3\) to 348.32 Å\(^3\) with increasing Ce content from \( x = 0 \) to 0.3. The maximum value of \( V = 351.06 \text{ Å}^3 \) was obtained at \( x = 0.2 \). The maximum volume fraction (84 %) of the 1:12 phase was obtained for annealed sample with \( x = 0.2 \).
The unit cell volume of the main 1:12 phase for samples after nitriding non-monotonically increases from 350.02 Å³ to 357.24 Å³ with increasing Ce content from \( x = 0 \) to 0.3. The maximum value of \( V = 360.41 \) Å³ was obtained at \( x = 0.2 \). The maximum volume fraction (79 %) of the 1:12 phase was also obtained for annealed sample with \( x = 0.2 \) (see Table 3). The average value of the volume effect (the increase in the unit cell volume after nitriding) was obtained to be \( \approx 2.5 \) %.

Table 2. XRD data of the \((\text{Nd}_{0.6}\text{Ce}_{0.2}\text{Zr}_{0.2})(\text{Fe}_{0.75}\text{Co}_{0.25})_{1.3}\text{Ti}_{0.35}\text{V}_{0.35}\) alloys in the as-cast state

| Sample | Phase composition (Space group) | Content (vol. %) | Lattice parameters | Unit cell volume (V, Å³) |
|--------|----------------------------------|------------------|-------------------|-------------------------|
|        |                                  |                  | \( a, \) Å | \( c, \) Å | \( c/a \) |                      |
| \( x = 0 \) | \((\text{Nd, Ce})(\text{Fe, Co, Ti, V})_{12}\) (I4/mmm) | 72.0(7)          | 8.456(2) | 4.894(2) | 0.579 | 349.94(16) |
|         | \( \alpha-(\text{Fe, Co})\) (Im-3m) | 23.0(5)          | 2.876(4) | 2.876(2) | 1 | 23.79(37) |
|         | \((\text{Nd, Ce})(\text{Fe, Co})_{17}\) (R-3m) | 5.0(3)           | 8.483(7) | 12.537(8) | 1.478 | 781.31(98) |
| \( x = 0.1 \) | \((\text{Nd, Ce})(\text{Fe, Co, Ti, V})_{12}\) (I4/mmm) | 70.0(8)          | 8.434(4) | 4.889(2) | 0.580 | 347.77(69) |
|         | \( \alpha-(\text{Fe, Co})\) (Im-3m) | 20.0(4)          | 2.875(4) | 2.875(2) | 1 | 23.76(61) |
|         | \((\text{Fe, Co})(\text{Ti, V})\) (P6/mmc) | 3.0(4)           | 5.190(3) | 10.801(9) | 2.081 | 251.96(42) |
|         | \((\text{Nd, Ce})(\text{Fe, Co})_{17}\) (R-3m) | 7.0(9)           | 8.461(2) | 12.529(3) | 1.481 | 776.76(31) |
| \( x = 0.2 \) | \((\text{Nd, Ce})(\text{Fe, Co, Ti, V})_{12}\) (I4/mmm) | 62.0(9)          | 8.424(2) | 4.885(4) | 0.580 | 346.66(17) |
|         | \( \alpha-(\text{Fe, Co})\) (Im-3m) | 24.0(8)          | 2.878(7) | 2.878(7) | 1 | 23.84(10) |
|         | \((\text{Fe, Co})(\text{Ti, V})\) (P6/mmc) | 5.0(7)           | 5.352(9) | 8.060(2) | 1.506 | 200.01(17) |
|         | \((\text{Nd, Ce})(\text{Fe, Co})_{17}\) (R-3m) | 9.0(6)           | 8.485(2) | 12.552(2) | 1.480 | 782.90(21) |
| \( x = 0.3 \) | \((\text{Nd, Ce})(\text{Fe, Co, Ti, V})_{12}\) (I4/mmm) | 60.0(4)          | 8.413(3) | 4.879(9) | 0.580 | 345.33(14) |
|         | \( \alpha-(\text{Fe, Co})\) (Im-3m) | 27.0(4)          | 2.874(6) | 2.874(6) | 1 | 23.73(09) |
|         | \((\text{Fe, Co})(\text{Ti, V})\) (P6/mmc) | 5.0(8)           | 5.481(3) | 7.221(3) | 1.317 | 187.47(10) |
|         | \((\text{Nd, Ce})(\text{Fe, Co})_{17}\) (R-3m) | 10.0(2)          | 8.489(5) | 12.560(7) | 1.480 | 783.85(34) |

For example, Figure 2 shows X-ray diffraction patterns of the \((\text{Nd}_{0.6}\text{Ce}_{0.2}\text{Zr}_{0.2})(\text{Fe}_{0.75}\text{Co}_{0.25})_{11.3}\text{Ti}_{0.35}\text{V}_{0.35}\) sample after arc-melting, melt-spinning, annealing and nitriding (in different structural state).
3.3. Magnetic hysteresis properties

Magnetic hysteresis properties for the (Nd$_{0.8}$,Ce,Zr$_{0.2}$)(Fe$_{0.75}$Co$_{0.25}$)$_{11.3}$Ti$_{0.35}$V$_{0.35}$ alloys after melt spinning, annealing and nitriding (in different structural state)

| Sample | Phase composition               | Content (vol. %) | Lattice parameters | Unit cell volume (V, Å$^3$) |
|--------|--------------------------------|-----------------|-------------------|------------------|
|        |                                |                 | a, Å              | c, Å             | c/a              |                               |
| x = 0  | (Nd, Ce, Zr)(Fe, Co, Ti, V)$_{12}$ | 84.0(7)         | 8.445(2)          | 4.796(2)         | 0.568            | 342.04(18)                   |
|        | α-(Fe, Co)                      | 16.0(8)         | 2.880(9)          | 2.880(9)         | 1                | 23.89(13)                    |
| x = 0.1| (Nd, Ce, Zr)(Fe, Co, Ti, V)$_{12}$ | 86.0(5)         | 8.451(3)          | 4.833(4)         | 0.572            | 345.20(21)                   |
|        | α-(Fe, Co)                      | 14.0(1)         | 2.879(6)          | 2.879(6)         | 1                | 23.86(22)                    |
| x = 0.2| (Nd, Ce, Zr)(Fe, Co, Ti, V)$_{12}$ | 93.0(8)         | 8.480(2)          | 4.866(3)         | 0.574            | 350.02(16)                   |
|        | α-(Fe, Co)                      | 7.0(5)          | 2.878(5)          | 2.878(5)         | 1                | 23.84(11)                    |
| x = 0.3| (Nd, Ce, Zr)(Fe, Co, Ti, V)$_{12}$ | 88.0(4)         | 8.477(2)          | 4.836(2)         | 0.570            | 347.51(14)                   |
|        | α-(Fe, Co)                      | 12.0(9)         | 2.877(2)          | 2.877(2)         | 1                | 23.81(21)                    |

annealed

| Sample | Phase composition               | Content (vol. %) | Lattice parameters | Unit cell volume (V, Å$^3$) |
|--------|--------------------------------|-----------------|-------------------|------------------|
| x = 0  | (Nd, Ce, Zr)(Fe, Co, Ti, V)$_{12}$ | 73.0(4)         | 8.456(6)          | 4.812(4)         | 0.569            | 344.08(14)                   |
|        | α-(Fe, Co)                      | 27.0(7)         | 2.876(7)          | 2.876(7)         | 1                | 23.79(11)                    |
| x = 0.1| (Nd, Ce, Zr)(Fe, Co, Ti, V)$_{12}$ | 75.0(4)         | 8.460(3)          | 4.842(3)         | 0.572            | 346.59(31)                   |
|        | α-(Fe, Co)                      | 25.0(7)         | 2.874(5)          | 2.874(5)         | 1                | 23.75(4)                     |
| x = 0.2| (Nd, Ce, Zr)(Fe, Co, Ti, V)$_{12}$ | 84.0(5)         | 8.486(8)          | 4.875(2)         | 0.575            | 351.06(15)                   |
|        | α-(Fe, Co)                      | 16.0(3)         | 2.873(4)          | 2.873(4)         | 1                | 23.72(67)                    |
| x = 0.3| (Nd, Ce, Zr)(Fe, Co, Ti, V)$_{12}$ | 76.0(5)         | 8.479(2)          | 4.845(6)         | 0.571            | 348.32(19)                   |
|        | α-(Fe, Co)                      | 24.0(3)         | 2.872(7)          | 2.872(7)         | 1                | 23.69(11)                    |

nitried

| Sample | Phase composition               | Content (vol. %) | Lattice parameters | Unit cell volume (V, Å$^3$) |
|--------|--------------------------------|-----------------|-------------------|------------------|
| x = 0  | (Nd, Ce, Zr)(Fe, Co, Ti, V)$_{12}$ | 68.0(8)         | 8.525(2)          | 4.823(2)         | 0.566            | 350.52(18)                   |
|        | α-(Fe, Co)                      | 32.0(5)         | 2.874(9)          | 2.874(9)         | 1                | 23.74(13)                    |
| x = 0.1| (Nd, Ce, Zr)(Fe, Co, Ti, V)$_{12}$ | 70.0(5)         | 8.552(6)          | 4.868(8)         | 0.569            | 355.88(71)                   |
|        | α-(Fe, Co)                      | 30.0(1)         | 2.873(7)          | 2.873(7)         | 1                | 23.71(91)                    |
| x = 0.2| (Nd, Ce, Zr)(Fe, Co, Ti, V)$_{12}$ | 79.0(7)         | 8.578(3)          | 4.898(4)         | 0.571            | 360.41(31)                   |
|        | α-(Fe, Co)                      | 21.0(8)         | 2.872(8)          | 2.872(8)         | 1                | 23.69(31)                    |
| x = 0.3| (Nd, Ce, Zr)(Fe, Co, Ti, V)$_{12}$ | 72.0(4)         | 8.570(9)          | 4.864(5)         | 0.568            | 357.24(12)                   |
|        | α-(Fe, Co)                      | 28.0(9)         | 2.870(8)          | 2.870(8)         | 1                | 23.64(15)                    |
Magnetic hysteresis properties at room temperature of samples after nitriding were obtained for sample with x = 0.2. The increase in the magnetic hysteresis properties at room temperature of samples after nitriding is likely to be related to the volume effect of the main 1:12 phase.

| Sample | Coercive force ($H_c$, kA/m (Oe)) | Remanence magnetization ($\sigma_r$, A·m²/kg) | Saturation magnetization ($\sigma_s$, A·m²/kg) |
|--------|----------------------------------|---------------------------------|---------------------------------|
| as-cast | | | |
| x = 0   | 8.8 (110)                        | 5.5                             | 154                             |
| x = 0.1 | 8.7 (109)                        | 5.2                             | 152                             |
| x = 0.2 | 7.3 (92)                         | 5.1                             | 151                             |
| x = 0.3 | 7.0 (88)                         | 5.0                             | 150                             |
| melt-spun | | | |
| x = 0   | 20.5 (258)                       | 16.0                            | 143                             |
| x = 0.1 | 22.7 (285)                       | 16.4                            | 144                             |
| x = 0.2 | 28.4 (357)                       | 18.5                            | 145                             |
| x = 0.3 | 24.6 (309)                       | 17.3                            | 144                             |
| annealed at 700 °C for 15 min | | | |
| x = 0   | 20.6 (259)                       | 16.1                            | 145                             |
| x = 0.1 | 23.3 (293)                       | 16.6                            | 147                             |
| x = 0.2 | 28.9 (364)                       | 18.7                            | 151                             |
| x = 0.3 | 24.8 (312)                       | 17.9                            | 148                             |
| nitrided | | | |
| x = 0   | 28.8 (362)                       | 24.6                            | 150                             |
| x = 0.1 | 32.7 (411)                       | 25.1                            | 152                             |
| x = 0.2 | 56.8 (714)                       | 34.2                            | 157                             |
| x = 0.3 | 40.5 (509)                       | 28.5                            | 154                             |

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 of grains and level of microdeformations).

4. Conclusions

We have obtained the magnetic material from the (Nd$_{0.8-x}$Ce$_x$Zr$_{0.2}$)(Fe$_{0.75}$Co$_{0.25}$)$_{11.1}$Ti$_{0.15}$V$_{0.35}$ alloys by arc-melting, melt-spinning, annealing and nitriding. The volume fraction of compound with the ThMn$_{12}$-type structure after melt-spinning, annealing, and nitriding non-monotonically increases from 84 % to 88 %, from 73 % to 76 %, and from 68 % to 72 % with increasing Ce content from x = 0 to 0.3, respectively. Almost single-phase samples with the average grain size of 120-180 nm. were produced by melt-spinning. The maximum volume fraction (93 %) of the main 1:12 phase was observed for the as-spun sample with x = 0.2.

The optimal magnetic hysteresis properties at room temperature were obtained for sample with x = 0.2 subjected to combined treatment that includes the melt-spinning, annealing, and nitriding; the reached magnetic properties are $H_c = 56.8$ kA/m (714 Oe), $\sigma_r = 34.2$ A·m²/kg, $\sigma_s = 157$ A·m²/kg.
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