Structure and magnetic properties of melt-spun ribbons of Sm(Co,Fe,Cu,Zr)z with high cobalt content

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Abstract. In this work the investigation of structure and magnetic properties of SmCo7.5Fe3.09Cu0.84Zr0.3 and SmCo7.52Fe3.01Cu0.84Zr0.28 melt-spun ribbons with high cobalt content after different heat treatments was performed. The phase composition and magnetic properties of the samples were determined. Isothermal aging at 600-800 °C with subsequent slow cooling leads to the slight increase in coercivity of the samples. After arc-melting the phase composition of the samples is hexagonal Sm2Co17 and CoFe. After melt-spinning a small amount of the disordered SmCo5 phase is detected. After aging metastable SmCo5 disappears, and the phase structure is basically hexagonal phase Sm2Co17 and CoFe, except a tiny amount of SmCo5 and rhombohedral Sm2Co17 after aging at 800 °C. Magnetic properties of the samples are relatively low because the phases, essential for the high-coercive state in these alloys, do not form during applied heat treatments.

1. Introduction
Nowadays hard magnetic materials are widely used in different fields, such as health, electronics, military, automotive industry, production of motors and generators. Three generation of permanent magnets, SmCo5, Sm2Co17 and Nd-Fe-B, have been developed [1]. Nd-Fe-B magnets have the highest magnetic energy product, while SmCo5 and Sm2Co17 have the highest value of the coercivity and Curie temperature. Significant progress has been made recently on the development of Sm(Co,Fe,Cu,Zr)x sintered magnets for high temperature application [2,3]. But in the last decades the values of (BH)max and coercivity, which had been achieved in permanent magnet materials before, haven’t grown considerably. One of the possible ways of the magnetic properties improvement is nanostructuring. Magnetic nanostructures can be produced by melt spinning, high energy ball milling, mechanochemical processing and so on [4].

Panagiotopoulos et al. [5] reported that by applying to melt spun Sm(Co0.74Fe0.10Cu0.12Zr0.04)8 ribbons an annealing process similar to the heat treatment used for sintered magnets, an analogous cellular microstructure can be obtained. Compared to the bulk materials, lower annealing temperatures and shorter heat treatment times were required. In samples containing Cu the increase of the wheel velocity leads to the rise of the Sm(Co0.74Fe0.10Cu0.12Zr0.04)8 alloy’s coercivity up to 10.5 kOe after annealing at 750°C. Interestingly, the cell structure of annealed ribbons is much smaller than the precipitation-like structure of the as-spun sample. The precipitation hardening results in an increase of the coercivity because the precipitates act as pinning centers. In general, rapid solidification of Sm2Co17-based alloys offers the possibility of achieving novel microstructures and with high coercivity. The changes in Sm
content in Sm(Co,Cu,Fe,Zr)11 ribbons may result in changes of the phase composition and microstructure of melt spun alloys and the exchange coupled nanocomposite formation [6]. However, the impact of alloys composition and melt-spinning parameters on structure and magnetic properties of Sm-Co magnets is covered in the literature insufficiently.

Another problem in the permanent magnet production is that high price of the rare-earth metals leads to the necessity to find ways to reduce rare earth content in the alloys for hard magnetic materials. In this case there are two methods to obtain the material with high magnetic properties: to substitute rare earth with more abundant elements or to find new compounds with different microstructure. From this point of view the Sm-Co compounds with high cobalt content attract a great interest. At first, the intermetallic phases with ThMn12 structure with high magnetocrystalline anisotropy energy (MAE) can form in these materials. Addition of doping elements results in further growth of MAE and in stabilization of the compound. Theoretical investigation of intermetallic ThMn12 shows that compounds containing Sm as RE element can have very promising properties [6]. In [7-9] the authors received Sm(Fe,Co)12-xTx alloys with good properties, doping alloys with Zr, which is used for substitution of the rare-earth element. At second, nanostructuring also can be a way to lesser the content of rare-earth elements in final product [2].

In this work we report on the structural and magnetic properties of rapidly quenched Sm(Co0.75Fe0.28Cu0.08Zrx)11 ribbons with high cobalt content, depending on heat treatment mode, and investigate the possibility of the exchange coupled nanocomposite production.

2. Materials and methods
The as-cast alloys with chemical compositions SmCo7.3Fe1.09Cu0.84Zr0.3 (1) and SmCo7.5Fe1.01Cu0.8zuZr0.28 (2) were obtained from high-purity components via arc-melting process in argon atmosphere. Then the rapidly quenched ribbons were obtained using melt-spinning technology. The samples were melt-spun in high purity argon atmosphere on a copper wheel at 40 m/s. All the melt-spun samples were milled into powder, heated to the aging temperature (600, 700, 800 °C), isothermally aged for and slow cooled in furnace (average cooling speed was 10 °C/min). The chemical compositions of the alloys after arc melting are given in the table 1.

| Sample 1 | Sample 2 |
|----------|----------|
| Mass. %  | At. %    | Mass. %  | At. %    |
| Sm       | 17.78    | 7.85     | 17.88    | 7.90     |
| Co       | 52.26    | 58.91    | 52.72    | 59.44    |
| Fe       | 20.42    | 24.29    | 20.01    | 23.80    |
| Cu       | 6.32     | 6.61     | 6.37     | 6.66     |
| Zr       | 3.22     | 2.34     | 3.02     | 2.20     |

X-ray fluorescence spectrometry method was applied to determine chemical composition of the arc-melted alloys. Magnetic properties were measured using vibrating sample magnetometer in magnetization field 25 kOe. Heat treatments were carried out in vacuum furnace equipped with cooling system. X-ray diffraction analysis was carried out to investigate phase composition of the samples. XRD spectra were collected with the diffractometer using monochromatized Co Ka radiation.

3. Results and discussion
The magnetic properties of the samples depending on the heat treatment mode are given in the tables 2 and 3. The samples have almost similar properties after similar treatments. After arc-melting coercivity Hc, specific residual magnetization σr, and specific saturation magnetization σs have the minimal values.
After melt spinning the magnetic properties rise considerably ($H_c$ and $\sigma_r$ grow almost twice). Despite expectations, aging does not result in huge growth of coercivity. Slow cooling (1.7 °C/min) after annealing at 800 °C does not lead to an improvement, but to a decrease in the coercive force, however, saturation magnetization reaches the peak. A considerable drop of the sample coercivity after slow cooling can be probably explained with oxidation process, nevertheless, further exploration is needed.

### Table 2. Magnetic properties of the sample 1 after various heat treatments.

| Heat treatment mode                      | $H_c$, kOe | $\sigma_r$, emu/g | $\sigma_s$, emu/g |
|-----------------------------------------|------------|-------------------|-------------------|
| Arc melting                             | 0.232      | 6.37              | 84.65             |
| Melt spinning                           | 0.418      | 12.89             | 89.95             |
| Melt spinning + 800 °C 1 h + cooling 10 °C/min | 0.410      | 14.85             | 93.31             |
| Melt spinning + 700 °C 1 h + cooling 10 °C/min | 0.417      | 14.66             | 93.47             |
| Melt spinning + 600 °C 1 h + cooling 10 °C/min | 0.465      | 14.89             | 92.9              |
| Melt spinning + 800 °C 1 h + cooling 1.7 °C/min | 0.19       | 11.31             | 136               |

### Table 3. Magnetic properties of the sample 2 after various heat treatments.

| Heat treatment mode                      | $H_c$, kOe | $\sigma_r$, emu/g | $\sigma_s$, emu/g |
|-----------------------------------------|------------|-------------------|-------------------|
| Arc melting                             | 0.183      | 5.79              | 84.65             |
| Melt spinning                           | 0.394      | 11.97             | 92.82             |
| Melt spinning + 800 °C 1 h + cooling 10 °C/min | 0.432      | 14.85             | 101               |
| Melt spinning + 700 °C 1 h + cooling 10 °C/min | 0.460      | 14.94             | 101               |
| Melt spinning + 600 °C 1 h + cooling 10 °C/min | 0.509      | 16.44             | 96.84             |
| Melt spinning + 800 °C 1 h + cooling 1.7 °C/min | 0.17       | 10.78             | 144               |

The results of the XRD analysis are provided on the in the tables 4 and 5 respectively. Hexagonal phase Sm$_2$Co$_{17}$ and CoFe phase exist after arc-melting in the alloys. After melt-spinning samples consist of hexagonal phase Sm$_2$Co$_{17}$ and CoFe with small amount of the disordered SmCo$_7$ phase. After annealing the phase structure changes slightly: at 800°C hexagonal Sm$_2$Co$_{17}$ and CoFe phases present, also a tiny amount of SmCo$_3$ and rhombohedral Sm$_2$Co$_{17}$ phases appear. After annealing at 700 and 600 °C there are only hexagonal phase Sm$_2$Co$_{17}$ and CoFe. The content of soft-magnetic phase varies from 14 to almost 27 mass %.

### Table 4. The results of X-ray diffraction analysis for sample 1.

| Heat treatment                        | Sm$_2$Co$_{17}$ H | CoFe | Sm$_2$Co$_{17}$ R | SmCo$_7$ | SmCo$_3$ |
|---------------------------------------|--------------------|------|-------------------|----------|----------|
| Arc melting                           | 79.4               | 20.6 | -                 | -        | -        |
| Melt spinning                         | 46                 | 12.8 | -                 | 41.2     | -        |
| Melt spinning + 800 °C 1 h + cooling 10 °C/min | 78.6               | 16.2 | 2.4               | -        | 2.8      |
| Melt spinning + 700 °C 1 h + cooling 10 °C/min | 73.3               | 26.7 | -                 | -        | 7.3      |
| Melt spinning + 600 °C 1 h + cooling 10 °C/min | 78.5               | 14.2 | -                 | -        | 7.3      |

Due to the excess of Co the cell structure does not form in the observed alloys, so, there is only slight growth of magnetic properties after annealing. The soft-magnetic CoFe phase has negative impact on
magnetic properties of the both samples. Soft-magnetic precipitations inhibit high properties achievement because they contribute to resulting value of coercivity and remanence.

**Table 5.** The results of X-ray diffraction analysis for sample 2.

| Phase, mass. % | Sm$_2$Co$_{17}$ H | CoFe | Sm$_2$Co$_{17}$ R | SmCo$_7$ | SmCo$_5$
|---------------|-----------------|------|-----------------|----------|----------|
| Arc melting   | 79.6            | 20.4 | -               | -        | -        |
| Melt spinning | 24.0            | 11.1 | -               | -        | -        |
| Melt spinning + 800 °C 1 h + cooling 10 °C/min | 78.1 | 19.1 | - | 64.9 | - |
| Melt spinning + 700 °C 1 h + cooling 10 °C/min | 74.2 | 25.8 | - | - | 2.8 |
| Melt spinning + 600 °C 1 h + cooling 10 °C/min | 77.5 | 15.0 | - | - | 7.5 |

The so-called platelet Z-phase, enriched with Zr and forming in bulk Sm-Co-Fe-Cu-Zr magnets, has not been detected via XRD-analysis, probably due to its small content and very thin precipitations. The peak at 38°, related to (102) line in the rhombohedral Sm$_2$Co$_{17}$ phase, presents only on the spectra of sample 1 after aging at 800°C and cooling 10°C/min. Consequently, in other samples Sm$_2$Co$_{17}$ exists in a hexagonal modification.

Metastable phase SmCo$_{12}$ has not been detected in the microstructure of the investigated ribbons, which can be explained with different mechanisms of substitution, comparing doping elements in the studied alloys and in the compositions reviewed in [3-6], despite Zr addition, which should stabilize the Fe- and Co-rich ThMn$_{12}$-type phase.

The XRD spectra of the samples 1 and 2 are shown on the figures 1 and 2, respectively.

![Figure 1](image_url)  
*Figure 1. XRD spectra of the sample 1 (SmCo$_7$Fe$_{3.19}$Cu$_{0.84}$Zr$_{0.3}$) after different heat treatments.*
Figure 2. XRD spectra of the sample 2 \((\text{SmCo}_{7.52}\text{Fe}_{3.01}\text{Cu}_{0.84}\text{Zr}_{0.28})\) after different heat treatments.

On the figure 3 and 4 the hysteresis loops of the both samples are provided. It is interesting that the coercivity remains relatively low after melt-spinning and aging, but the remanence grows twice after melt-spinning. It probably can be explained with the metastable \text{SmCo}\textsubscript{7} precipitation.

Figure 3. The hysteresis loops of the sample 1 \((\text{SmCo}_{7.5}\text{Fe}_{3.09}\text{Cu}_{0.84}\text{Zr}_{0.3})\) after different treatments.
4. Conclusion
In this study the investigation of the structure formation in melt-spun Sm(Co,Fe,Cu,Zr)_{12} ribbons with high cobalt content was done. The obtained results for arc-melted samples are in good agreement with the previous studies: the existence of two phases in Co-high region at high temperatures was approved. Although the wide range of heat treatments was applied to enhance the magnetic properties of the ribbons, the coercivity of the samples remained low after aging. From the one hand, the cell structure, which is strongly related to high-coercive state forming both in bulk and melt-spun samples, does not occur due to the lack of Sm. From the other hand, the phase with the ThMn_{12} structure, which has the promising properties and forms in Sm(Fe,Co)_{12-x}M_{x}, alloys doping alloys with Zr, does not appear in the samples. Also, the precipitations of the soft magnetic CoFe phase have a negative impact on coercivity of the ribbons. However, the investigated alloys can be a promising materials for nanocomposite production due to high soft-magnetic phase content. Further exploration is needed for the magnetic properties’ improvement.

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