Influence of Severe Plastic Deformation on Magnetic Properties of Fe$_{48}$Ni$_{48}$Zr$_4$, Fe$_{49.5}$Co$_{16.5}$B$_{33}$Ta and Co$_{80}$Zr$_{16}$B$_4$ Alloys

S. Taskaev$^{1,2}$*, K. Skokov$^1$, V. Khovaylo$^{1,2,3}$, D. Gunderov$^4$, D. Karpenkov$^1$

$^1$Chelyabinsk State University, Chelyabinsk 454001, Russia
$^2$National University of Science and Technology "MISiS", Moscow 119049, Russia
$^3$ITMO University, St. Petersburg 197101, Russia
$^4$Ufa State Aviation Technical University, Ufa 450000, Russia

tsv@csu.ru

Abstract
This work reports the influence of high pressure torsion (HPT) on magnetic properties of Fe$_{48}$Ni$_{48}$Zr$_4$, Fe$_{49.5}$Co$_{16.5}$B$_{33}$Ta and Co$_{80}$Zr$_{16}$B$_4$ alloys. High degree of the plastic deformation dramatically affects microstructure of the samples by reducing the grain size down to the nanometer scale. No significant change in magnetic properties was observed for of Fe$_{48}$Ni$_{48}$Zr$_4$ and Fe$_{49.5}$Co$_{16.5}$B$_{33}$Ta alloys before and after heat treatment while an increase of the coercivity up to 2.25 kOe was found in the Co$_{80}$Zr$_{16}$B$_4$ sample after the heat treatment procedure. The origin of the coercivity increase lies in refined grain structure which was developed during HPT.

Keywords: Rare earth free permanent magnets, high pressure torsion, magnetic anisotropy, coercivity.

1 Introduction

Since the development of Nd–Fe–B magnets, rare-earth magnets have been essential components in many fields of technology because of their ability to provide a strong magnetic flux. Nevertheless, the dramatic increase in the price of rare-earths during last few years has renewed interest to the rare-earths free permanent magnets (Lewis, 2013).

The important properties of a permanent magnet include its coercivity, remanence and energy product. For a thorough explanation see, for instance, the textbook by Coey (Coey, 2010). There are essentially two means of achieving the large values of these properties necessary for today’s applications. First, the microstructure of a material can be optimized (in our case with the help of high pressure torsion) to prevent the rotation of ferromagnetic domains. The second factor is the intrinsic spin–orbit coupling of electrons that force spins to align along a particular crystallographic orientation,
giving rise to the magnetocrystalline anisotropy energy of a material. Because the strength of spin-orbit coupling increases as the fourth power of an element’s atomic number, maximizing the magnetocrystalline anisotropy energy is accomplished by utilizing heavier elements.

In our work we choose the objects of the investigation based of the following reasons.

1. The meteoritic tetrataenite Fe$_{50}$Ni$_{50}$ has the outstanding magnetic properties as a rare-earth free permanent magnet (Lewis, 2013), but the synthesis of this phase is extremely difficult. First-principle calculations show the effects of transition-metal and metalloid additions on the intrinsic magnetic properties of the $L1_0$-ordered FeNi (tetrataenite). Such additives may become useful to facilitate the formation of the tetrataenite phase, but the calculations indicate that their effect on the magnetic properties is mostly neutral or negative. There are, however, some exceptions, specifically, substitution of Fe and addition of the interstitial B to the structure (Manchanda, 2014). Preparation of rapidly quenched alloys Fe$_{48}$Ni$_{48}$X$_4$ (X=Ta, Zr, W, Mo, Re) showed that the Fe$_{48}$Ni$_{48}$Zr$_4$ sample exhibits the highest coercivity (Manchanda, 2014).

2. (Fe, Co)$_2$B alloys have an easy-axis anisotropy (Kuz’min, 2014). After preparation of rapidly quenched (Fe, Co)$_2$B alloys with a small addition of some chemical elements, the highest coercivity was observed for a Fe$_{49.5}$Co$_{16.5}$B$_{33}$Ta composition (see Fig.1). As is seen, in this compound the coercivity is at least 5 times larger than in the other compounds.

3. Co$_{80}$Zr$_{20}$ is a rare earth free permanent magnet material with coercivity around 3 kOe and magnetization around 80 Am$^2$kg$^{-1}$. Addition of boron enhances coercivity in this compound. There are few works where the magnetic properties of rapidly quenched Co$_{80}$Zr$_{16}$B$_4$ were investigated and it was shown that the coercivity is enhanced after heat treatment (Ghemawat, 1989 and Saito, 2013). The crystalline alloys with Zr content of 16 and 18 at.% have a coercive force exceeding 3 kOe. Slow-cooled samples of the same composition showed the coercivity of about 100 Oe. However, with increasing Zr concentration, the microcrystalline phases were found to exhibit good hard magnetic...
properties. These preliminary results suggest the possibility of making hard magnets with reduced concentrations of expensive rare-earth elements by replacing them with other elements. The formation of high coercive state during rapid solidification means a strong correlation between the microstructure and the hard magnetic properties, especially in the case of Co$_{80}$Zr$_{16}$B$_4$ alloy.

2 Sample preparation and characterization

HPT (Bridgeman anvils) was performed under 5GPa pressure with 5 complete turns at room temperature. Initial dimensions of the samples were 10 mm in diameter and 1.5 mm width. After HPT the widths of the alloys were 140, 380 and 250 micrometers for Fe$_{48}$Ni$_{48}$Zr$_4$, Fe$_{49.5}$Co$_{16.5}$B$_{33}$Ta, Co$_{80}$Zr$_{16}$B$_4$ correspondingly (see Fig. 2). Such high plastic deformation dramatically affects on microstructure of the samples and reducing the grain size up to nanometer scale.

The X-ray (Brucker D8 Advance) data (Fig. 3) show that HPT drives the Fe$_{49.5}$Co$_{16.5}$B$_{33}$Ta and Co$_{80}$Zr$_{16}$B$_4$ samples in an amorphous-like state while Fe$_{48}$Ni$_{48}$Zr$_4$ is still in the crystallized state. No foreign phases or impurity elements were detected by EDX (JEOL JSM–6010 LV) investigations.

3 Magnetic properties

Magnetic properties of the samples were measured by a Quantum Design MPMS-5S (SQUID). Field and temperature dependences of magnetization of the studied samples are shown in Figs. 4-6. Magnetization of each sample was measured just after HPT and after a heat treatment procedure. The
heat treatment procedure consisted in heating of the samples up to 1000 K with 2 K/s followed by cooling down to room temperature.

No significant change in the magnetization curves was observed for Fe$_{48}$Ni$_{48}$Zr$_4$ and Fe$_{49.5}$Co$_{16.5}$B$_{33}$Ta alloys before and after the heat treatment (see Figs. 4 and 5). The coercivity of Fe$_{48}$Ni$_{48}$Zr$_4$ does not exceed 100 Oe in both (HPT and annealed) cases (Fig. 4). The hysteresis seen on the temperature dependences of magnetization of Fe$_{48}$Ni$_{48}$Zr$_4$ is connected with $\alpha \rightarrow \gamma$ phase transition.

After HPT and the subsequent heat treatment procedure we do not observe any peculiarities inherent to the $L_1_0$ tetrataenite phase of Fe-Ni alloy. Formation of that phase is based on a long scale heat treatment procedure near the temperature of ordering from $A1$ chemical disordered to the $L1_0$ chemical ordered crystal structure of Fe-Ni. A high density of defects should increase kinetics of such diffusive phase transition and significantly reduce time for the formation of a high coercive state. Nevertheless, it has to be noticed here that idea that additions of interstitial boron atoms positively affect tetrataenite phase formation (Manchanda, 2014) was not supported by our experimental results.

Temperature and field dependences of magnetization of Fe$_{49.5}$Co$_{16.5}$B$_{33}$Ta sample are shown in Fig. 5. Smaller values of the magnetization for heating curve as compared with cooling curve point to a partial recrystallization of the sample from amorphous to microcrystalline state. It is found that the coercivity of Fe$_{49.5}$Co$_{16.5}$B$_{33}$Ta after HPT is equal to 130 Oe and tends to decrease down to 80 Oe after the heat treatment. Severe plastic deformation does not increase the coercive force, but shows a weak reverse effect of decreasing hysteresis loop by 40%.

Figure 4: Magnetization curves for Fe$_{48}$Ni$_{48}$Zr$_4$ alloy treated by HPT: temperature dependences (left); field dependences (right).

Figure 5: Magnetization curves for Fe$_{49.5}$Co$_{16.5}$B$_{33}$Ta alloy treated by HPT: temperature dependences (left); field dependences (right).
During heating the Co$_{80}$Zr$_{16}$B$_4$ sample undergoes a recrystallization from amorphous phase into a crystalline one with higher magnetization saturation (Fig. 6). It is found that after HPT and heat treatment procedure the coercivity force is increased up to 1.125 kOe at room temperature. Measurements at helium temperature showed that the coercivity is equal to 2.25 kOe, pointing to good hard magnetic properties of the sample. However, this value is smaller by 30% than that observed in rapidly quenched Co$_{80}$Zr$_{16}$B$_4$ alloys (Ghemawat, 1989). Boron addition positively affects on hard magnetic properties of some well-known hard magnetic alloys such as RE$_2$TM$_{14}$B (where RE – rare earths elements, TM – transitional metals) by the formation of finely dispersed intermetallic phases. Boron here plays a role of a driver of amorphization process.

In the investigated composition, the presence of the intermetallic Co$_{11}$Zr$_2$ and Co$_2$Zr phases is energetically more profitably in the case of HPT treated sample than in the as cast state. In the plastically deformed sample the presence of finely dispersed second phases obviously prevents grain coarsening. In the resulting inhomogeneous microcrystalline structure the mobility of domain walls is decreased thus ensuring good hard magnetic properties.

**Figure 6:** Magnetization curves for Co$_{80}$Zr$_{16}$B$_4$ alloy treated by HPT: temperature dependences (left); field dependences (right).

### 4 Conclusion

It is shown that HPT affects magnetic properties of 3$d$ compounds in different ways and in some cases it is possible to enhance the coercivity.

1) Neither an increase of the coercivity nor tetrataenite reflexes were found in Fe$_{48}$Ni$_{48}$Zr$_4$ after HPT.
2) In the case of Fe$_{49.5}$Co$_{16.5}$B$_{33}$Ta a decrease of the coercivity was observed after HPT.
3) In HPT sample of Co$_{80}$Zr$_{16}$B$_4$ the value of coercive force is equal to 2.25 kOe at liquid helium temperature which is comparable with previous results (Ghemawat, 1989 and Saito, 2013), where this compound was prepared by melt spinning technique. The origin of the coercivity enhancement lies in refining grain structure which has been amorphised during HPT.

Although the energetic product of the best Co$_{80}$Zr$_{16}$B$_4$ alloy is not large due to moderate values of the magnetization and mostly not comparable to those of the best commercial hard magnets, the present investigation illustrates the possibilities of significant improvement of hard magnetic properties of the investigated samples by severe plastic deformation. A nanostructured state, which can be achieved with the help of HPT, is suggested to be a promising method for the formation of a high coercivity state in some rare-earth free compounds.
Acknowledgements

Authors gratefully acknowledge the financial support of the Ministry of Education and Science of the Russian Federation in the framework of Increase Competitiveness Program of MISiS, the financial support of the RF President MD-770.2014.2 and RSF 15-12-10008 grants. Magnetic measurements were performed due to Russian Science Foundation financing (project 15-12-10008).

References