Effect of Cr, C, B and Mo substitutions on the structure and magnetic properties of Zr-Co Rare-Earth-free magnetic alloy

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Abstract. Acquiring new permanent magnets without Rare-Earths is a new challenge in the field of magnetic materials and Co-rich Co-Zr alloys seem to be a solution to be pursued. The microalloying effects of different elements on the structure and stabilization of hard magnetic Zr\textsubscript{2}Co\textsubscript{11} phase of Zr-Co alloy have been analysed in the past and it was shown that the Zr\textsubscript{2}Co\textsubscript{11} non-cubic high anisotropy structure can be stabilized by the partial substitution of Co in the ZrCo alloy with elements with high atomic radius. In the present work, we made substitutions of up to 5\% alloying elements such as Mo, C, B, Cr in order to highlight how the element with the small / large atomic radius stabilize the nano-hard magnetic phase. The structural and magnetic properties of the new Zr\textsubscript{18}Co\textsubscript{77}Cr\textsubscript{3}X\textsubscript{2} (X = C, B, Mo) prepared bulk alloys have been analysed and related to those of the original Zr\textsubscript{13}Co\textsubscript{87}.

1. Introduction

The exponential development of science and technology, and the need for magnetic energy, make strong magnets indispensable. At the base of many magnetic materials are rare earths (RE). However, the current geopolitical and geostrategic context, as well as the RE high costs, make it imperative to find magnetic materials without rare earths for strong permanent magnets. Since, fundamentally, this is not impossible researchers from all over the world are looking for alternatives.

To obtain a permanent magnet with high energy product (BH)\textsubscript{max} one has to start from a material with a high Curie temperature, a large saturation magnetization and an appreciable magnetic anisotropy. The first two requirements are fulfilled by the 3d- elements that are additionally cheap and affordable. The drawback of the 3d elements is their low magnetic anisotropy due to the weak spin-orbit coupling. However, there are ways to improve magnetocrystalline anisotropy like doping with elements to change the structure from cubic to tetragonal (e.g. Fe-N), by combining 3d elements with 5d and searching for new compounds or re-examination of less studied alloys [1]. Very good results have been obtained, for instance, in FePt alloys showing tetragonal L\textsubscript{1}o-ordered structure and a (BH)\textsubscript{max}=54 MGOe [2, 3], but the high cost of Pt limits its use for commercial applications. Mn-based alloys, like MnBi, MnAl, MnGa, are widely investigated due to their high constant of uniaxial anisotropy (K1) and Curie temperature (Tc), but up to now the published results are modest, the highest value for (BH)\textsubscript{max} being only 7.7 MGOe [4 - 9].

Recently, Co-rich transition metal Co\textsubscript{100-x}TM\textsubscript{x} alloys are reported as good candidates for the replacement of rare earth based magnetic materials. One of them is Co-Zr alloy, in which phase diagram is the metastable Co\textsubscript{11}Zr\textsubscript{2} phase formed by a peritectic reaction L + Zr\textsubscript{6}Co\textsubscript{23} \rightarrow Zr\textsubscript{2}Co\textsubscript{11} at high temperatures [10]. Recent experimental results have proved that the rhombohedral Zr\textsubscript{2}Co\textsubscript{11} has hard magnetic properties [11]. The Zr\textsubscript{2}Co\textsubscript{11} is polymorphic, having the pseudohexagonal, orthorhombic or rhombohedral crystalline structures, with closely competitive energies [12]. Applying a classical melting procedure of the component elements, the alloy is obtained in the cubic structure Co\textsubscript{23}Zr\textsubscript{6}, with soft magnetic properties. But, it was shown that the Zr\textsubscript{2}Co\textsubscript{11} non-cubic high anisotropy structure can be stabilized in ZrCo alloy by the partial substitution of Co with elements with high atomic radius [13].
Therefore we made substitutions of up to 5% of alloying elements like Mo, C, B, Cr in order to highlight the role of the atomic radius of the substitution elements in the nucleation and stabilization of hard magnetic phase. The structural and magnetic properties of new Zr_{18}Co_{77}X_{2} (X = C, B, Mo) prepared as bulk alloys have been analysed and related to those of Zr_{13}Co_{87}. Starting from the hard Zr_{2}Co_{11} phase with uniaxial anisotropy and high Curie temperature (500°C) but with low saturation magnetization at room temperature, the aim of this study is to achieve a potentially performing material for permanent magnets.

2. Experimental details

Bulk alloys with nominal compositions Zr_{13}Co_{87}, Zr_{18}Co_{77}Cr_{3}C_2, Zr_{18}Co_{77}Cr_3B_2, Zr_{18}Co_{77}Cr_3Mo_2, denoted in the following ZrCo, CrC, CrB and respectively CrMo, were prepared by arc melting in argon atmosphere from high purity (99.99%) constituent elements. In order to obtain a better homogeneity, the samples were re-melted four times.

The Diffractometer Bruker D8 Advance with Cu Kα radiation was used for the crystalline structure investigation. Magnetic measurements were made with a Quantum Design Physical Properties Measurement System (PPMS) working in vibrating sample magnetometry (VSM) mode.

3. Results and discussions

3.1. Structural characterization

The type and size of the unit cell of the polymorph Zr_{2}Co_{11} phase are still under debate. In bulk samples multiple phases and small grain size, that enlarge the diffraction lines, make difficult to determine the atomic crystalline structures of this compound using standard X-ray techniques. However, the development and optimization of this material for practical applications is conditioned by the clarification of its crystalline structure [12]. The XRD patterns recorded for ZrCo, CrC and CrB reveal the coexistence of cubic Zr_{6}Co_{23}, hexagonal Co – rich soft magnetic phases and Zr_{2}Co_{11} in orthorhombic symmetry. The crystallite size, calculated using the Scherrer formula, varies between 7 nm and 20 nm for ZrCo, CrC, CrB alloys. Diffraction maxima belonging to the rhombohedral phase appear in the diffractogram specific to the CrMo sample. Rhombohedral structure of hard magnetic phase Zr_{2}Co_{11} is often obtained for stoichiometry ZrCo_{5.1} [5].

![Figure 1. XRD pattern recorded at room temperature for all investigated samples.](image)

Based on Rietveld refinements using MAUD code [14] a small amount of ZrCo_{5.1} hard magnetic phase with rhombohedral structure (about 5%) was detected in CrMo sample, besides the main soft magnetic phase Co_{2.23}Zr_{0.77} with cubic structure (Fd-3m group, fitted lattice constant a=0.6857(5) nm and crystal size of 23(2) nm ) and the minority Co-rich phase with hexagonal structure (P63/mmc
group) with smaller crystal size of 10(1) nm. These values of the crystallite size agree well with that obtained by using Scherrer method.

![XRD Data](image)

**Figure 2.** Rietveld analysis of the XRD data for the sample denoted CrMo.

The presence in the early stage of the rhombohedral phase is the evidence that CrMo alloy is a good precursor for a hard magnetic material without rare earths.

### 3.2. Magnetic characterization

In Figure 3.a are presented the temperature dependences of magnetization measured in 2T for the under discussion alloys. It is to note the very slow magnetization increase with the temperature reduction especially for the reference alloy, suggesting a Curie temperature much higher than room temperature.

![Magnetization vs Temperature](image)

**Figure 3.** (a) The overall behavior of the Field Cooling (FC) curves measured in 2T applied magnetic field; (b) Hysteresis loops collected at 100K (empty symbols) and 300K (full symbols) in the field range from –80 kOe to 80 kOe for ZrCo, CrC and CrMo samples.

Hysteresis loops collected at 100K and 300K in the field range from -80 to 80 kOe on ZrCo, CrC and CrMo samples depicted in Fig.3b, show the high saturation field, meaning saturation of magnetization difficult to reach. This trend suggests a randomly oriented magnetic anisotropy mechanism (RMA). The nanometric dimensions of crystallites and the presence of a disordered spin
structure with large local anisotropy generate such random magnetic anisotropy behavior. Disordered systems with RMA show distribution of the anisotropy energies, which involve magnetic moments with different easy magnetization axes in various sites, due to local crystal fields. In addition, it is worth noting the decrease of magnetization in the CrC substitution alloy, which is even more pronounced in the CrMo substitution alloy. This behaviour suggests a non parallel coupling between the cobalt magnetic moments with those of the substitution atoms (Cr and Mo). Theoretical and experimental studies have revealed that RMA suppresses the ferromagnetic coupling of magnetic moments resulting a speromagnetic structure of spins. The large anisotropy randomly oriented owning to the random atomic arrangement strongly influences magnetic properties. If we analyze the hysteresis curves, in small fields is present the specific behavior of magnetic domains. At higher fields, the speromagnetic behavior is obvious: the magnetic moments disposed within a cone begin to orient in the direction of the applied field. It is worth mentioning here, that in the RMA, the speromagnetic behavior is defined by a $4\pi$ solid angle, meaning randomly oriented spins. Besides this local behavior, we also have an exchange interaction that is different from pure Co, because we do not only have Co atoms. Therefore, the high magnetization in the ZrCo sample is due to the strong exchange interaction through the direct spatial overlap of the 3d shells in the alloy, but is less than pure Co, due to Zr-induced 3d-4d hybridization. The hybridization differs depending on the substitution element, and in the other samples is added the hybridization due to substitutions of Cr, C, B and Mo.

From hysteresis loops it is evident the decrease of magnetization at saturation with the increase of atomic radius of substitution element. On the contrary, the coercive field increases with the increase of the radius of the substitution element. Room temperature hysteresis loops evidenced lower magnetization than those recorded at 100K. The magnetization diminishing can be justified by increased magnetic fluctuation when measuring temperature approaches Currie point. Additionally, low values of magnetization at saturation obtained for sample with substitutions can be the effect of the presence of oxides. According to RMA model, the bulk alloys exhibit a spin-glass-like behaviour, when the dimensions of the crystallites are located in the nanoscale region [13, 15, 16]. The nanometric crystallite size is also the justification for the small coercive fields in some alloys. According to the J. Löffler and W. Wagner's [17] regarding the relation between the crystallite size and magnetic properties, if the crystallite size is comparable to the effective domain-wall width of nanostructured bulk materials, the magnetization of neighboring grains may be aligned. The magnetocrystalline anisotropy constant is then averaged over several crystallite inducing a decrease of the coercive field with decreasing the crystallite size. As highlighted in insets of Fig. 4, the coercive field values are small, depending on the substitution elements, ranging from 20 Oe for ZrCo to 200 Oe for the CrMo sample. The coercive field increased by an order of magnitude compared to the others in the CrMo sample. The X-ray diffraction on the same sample reveals the appearance of the rhombohedral phase. So, we have proved that substitution with Mo, the element with the largest atomic radius of the elements chosen by us, is responsible for the occurrence of the rhombohedral phase, which give hard magnetic magnetic properties. This behaviour, together with the weak variation of magnetization vs temperature and the high value of the magnetic field required to achieve saturation, suggests that the RMA model explains the magnetic behavior of these alloys.

4. Conclusion
The presence of Random Magnetic Anisotropy and the behaviour of magnetization in high fields (saturation is difficult to reach) show that the material is a good precursor in order to obtain Permanent Magnets and can be used as a substitute for magnetic materials based on Rare Earths, after proper processing and thermal treatments.
Figure 4. (a) Hysteresis loops for ZrCo; the same for (b) CrC and (c) CrMo samples. The detail about coercitivity are shown in inset bottom right. In CrMo sample is obvious that the saturation of magnetizations is difficult to achieve.

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