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STRUCTURAL AND MAGNETIC PROPERTIES OF FERROMAGNETIC Co-Zr ALLOYS OBTAINED BY MECHANICAL ALLOYING

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ABSTRACT. The structural and magnetic properties of $Co_{11}Zr_2$ and $Co_{82}Zr_{12}$ ferromagnetic alloys, produced via the non-equilibrium synthesis method of mechanical alloying, were investigated. The formation of the magnetic phases was investigated at milling times of up to 20 h. As the powders became amorphous during the alloying process, annealing was performed to allow for a more thorough investigation of the crystalline structure of the resulting alloys. The magnetic properties of the final samples were investigated via demagnetization curves.

Keywords: *mechanical alloying, rare-earth free permanent magnets, Co-Zr hard magnetic phase.*

INTRODUCTION

Permanent magnets are essential in industrial and technological applications, however a major disadvantage is that the materials for high performance permanent magnets contain large quantities of rare earths, which are exploited and processed in only a few regions on the globe, a major downside for industry as supply could always be shut off or the price

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may inflate drastically in a short amount of time [1][2]. Therefore solutions to the dependence on rare earth materials are being sought. The $Co_{11}Zr_2$ hard magnetic phase has been proposed as a candidate material for rare-earth free permanent magnets [3-7], while the composition $Co_{82}Zr_{12}$ is a spring magnet [8] ($Co_{11}Zr_2$ as the hard magnetic phase and Co as the soft magnetic phase).

In this work we employ a non-equilibrium synthesis method, mechanical alloying (MA), in order to obtain the hard magnetic $Co_{11}Zr_2$ phase and hopefully exchange couple it with soft magnetic Co.

EXPERIMENTAL

The samples were made from elemental powders with the compositions $Co_{82}Zr_{12}$ and $Co_{11}Zr_2$. The powder mixtures were thoroughly mixed for half an hour, using a Turbula mixer and were then milled for up to 20 h in Fritsch Pulverisette 4 planetary ball mill, under purified Ar atmosphere. The ratio between the disk and planet speeds was 333 rpm/-900 rpm. The milling media is made of 440C steel. Nine 15 mm diameter balls were placed in each 80 ml steel vial which translates to an impact energy of 77 mJ/ball adding up to a total useful power of 5 W.

Differential scanning Calorimetry (DSC) measurements, carried out using a TA Instruments Q600 equipment, were done on the powders at different stages in the MA process.

The powders were annealed at 1030 °C for 7 days in order to ensure their homogeneity. The annealed samples were reheated to 1030 °C and kept there for 1 hour followed by quenching in water.

The structure of the samples was investigated by X-Ray diffraction (XRD) on a Bruker D8 Advance diffractometer equipped with a Cu Kα source.

The magnetic properties of the samples were investigated using a Cryogenics vibrating sample magnetometer, in applied fields of up to 4 T. The powder samples were blocked in epoxy resin for these measurements.

RESULTS AND DISCUSSION

DSC measurements were used to evaluate the MA process and to determine the annealing temperature required for the samples (Figure 1). After 2 h of MA we can see a large peak at low temperatures (convoluted signal from strain release and the phase transition of Co). Additional peaks are observed at high temperature due to the formation of various Co-Zr alloys. After 20 h MA we can see that only one sharp peak, at 620 °C, remains for the $Co_{11}Zr_2$ composition (Figure 1a), while for the $Co_{82}Zr_{12}$ samples we can still see a small peak (at 400 °C) indicative of the phase transition of Co (Figure 1b).

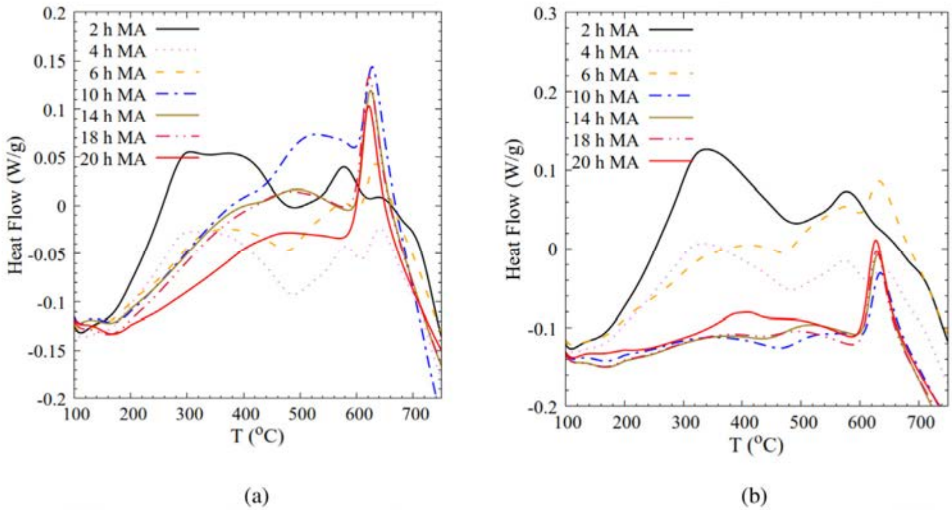

Figure 1. DSC curves for $Co_{11}Zr_2$ (a) and $Co_{82}Zr_{12}$ (b) MA powders at different milling times

The structure of the MA samples was investigated using XRD, Figure 2. We can see that for both compositions ($Co_{11}Zr_2$ and $Co_{82}Zr_{12}$), the samples become completely amorphous after 20 h MA, with only a very broad structure being visible. Because the 20 h MA powders seem to be fully alloyed, but amorphous, annealing at high temperature was used in order to recrystallize them.

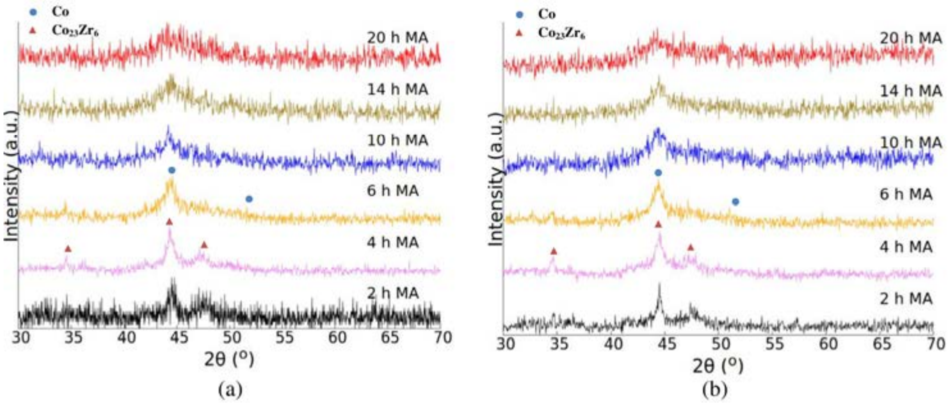

Figure 2. XRD patterns for the 2 to 20 h MA (a) $Co_{11}Zr_2$ and (b) $Co_{82}Zr_{12}$ powders

Two successive heat treatments were done on both samples: the samples were first annealed at 1030 °C for 7 days and slowly cooled to room temperature (TT), secondly a part of the powder was re-annealed at the same temperature for 1 hour and quenched in water (TT+Q). The fully crystalized samples (Figure 3) are multiphase (a mixture between Co, $Co_{11}Zr_2$ and $Co_{23}Zr_6$ phases), with quenching having made little difference. However we must note that the $Co_{82}Zr_{12}$ sample seems to have a higher concentration of the Orthorhombic $Co_{11}Zr_2$ phase, alongside the rhombohedral structure.

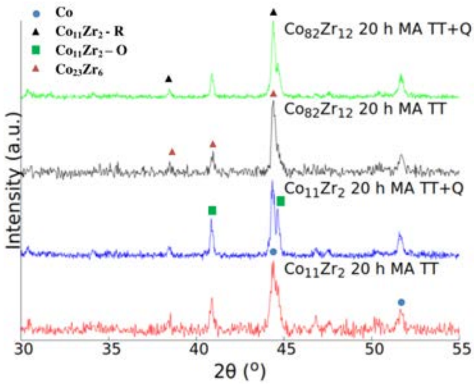

Figure 3. XRD patterns after annealing for the $Co_{11}Zr_2$ and $Co_{82}Zr_{12}$ compositions

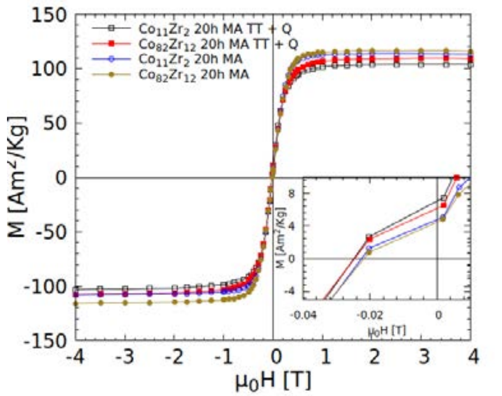

Figure 4. Demagnetization curves for the20 h MA and for annealed and quenched samples

Demagnetization curves, Figure 4, show little difference between the two compositions. The as-milled samples have very low remanence and coercivity (0.02 T). The annealing process improves these values by 25% and reduces saturation magnetization slightly, which leads us to conclude that by annealing the magnetic structure of the samples is hardened.

CONCLUSIONS

Mechanical alloying was investigated as a synthesis route for magnetic Co-Zr alloys, with potential applications as rare earth free permanent magnet materials. Even though the alloying process was effective, as determined via DSC and XRD measurements, the final alloys showed little coercivity and remanent magnetization, even after annealing.

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