

# The Structure and Magnetic Properties of $\text{Co}_{77}\text{Zr}_{18}\text{W}_5$ Melt-Spun Ribbons

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## ABSTRACT

Based on X-ray diffraction, microscopic and magnetic analysis, the structure and magnetic properties of  $\text{Co}_{77}\text{Zr}_{18}\text{W}_5$  melt-spun ribbons were studied in this paper. A new element to stabilize the metastable  $\text{Co}_5\text{Zr}$  phase was found and the coercivity observed in Co-Zr alloys can be obviously enhanced by proper tungsten substitution. The Curie temperature of  $\text{Co}_{77}\text{Zr}_{18}\text{W}_5$  ribbons is 475°C which suggests that W doped Co-Zr alloys may become an attractive candidate permanent magnets for practical applications in high temperature. Annealing of the  $\text{Co}_{77}\text{Zr}_{18}\text{W}_5$  ribbons results in a decrease of the coercivity which confirmed that the hard magnetic phase is  $\text{Co}_5\text{Zr}$  phase in  $\text{Co}_{77}\text{Zr}_{18}\text{W}_5$  melt-spun ribbons.

**Keywords:** Co-Zr Alloys;  $\text{Co}_5\text{Zr}$  Phase; Coercivity; Melt-Spun; Permanent Magnets

## 1. Introduction

To enhance the thermal stability of permanent magnetic materials for high temperature applications, recent developments are largely concentrated on the non-rare-earth containing permanent magnets in the magnet society. One of the candidates for the new permanent magnetic materials is Co-Zr system alloys [1]. In recently years, a great deal of effort has been devoted to improve the magnetic properties of Co-Zr system alloys by doping or optimizing the annealing conditions of rapidly quenched ribbons [2-5]. The reported maximum values of energy products in Co-Zr-B(-Si) melt-spun ribbons are comparable to those of the hard ferrites [6,7]. According to previous reports, either  $\text{Co}_5\text{Zr}$  phase or  $\text{Co}_{11}\text{Zr}_2$  phase is the hard magnetic phase in Co-Zr system alloys [7-11]. To further improve the hard magnetic properties of Co-Zr system alloys, it is essential to determine the hard magnetic phase in Co-Zr system alloys.

Previous studies show that the rapidly quenched Co-Zr-based alloys with near 18 at% Zr concentration have a good hard magnetic property. To our knowledge, works on Co-Zr system alloys were mostly performed by small atomic radius elements additions, such as B, Si or C [5]. In this work, we will broaden the range of admixture by doping the relatively large atomic radius tungsten element to Co-Zr alloys and focus on the structure and magnetic properties of  $\text{Co}_{77}\text{Zr}_{18}\text{W}_5$  melt-spun ribbons. Moreover, we will try to identify the hard magnetic phase in Co-Zr system alloys.

## 2. Experiment

The ingot of  $\text{Co}_{77}\text{Zr}_{18}\text{W}_5$  was prepared by arc melting the constituent elements, Co and Zr of purity 99.99% and W of purity 99.95%, in an arc furnace under argon atmosphere. To ensure homogeneity, the melting was carried out six times and the weight loss after the final melting was less than 0.3%. Then, small amounts of the alloy ingot were placed in a quartz crucible with an orifice of 0.8 mm at the bottom. The alloy ingot was induction melted in an argon atmosphere and then ejected through the orifice with argon on to a copper wheel rotating at a surface velocity ( $V_s$ ) of 40 m/s. The resultant melt-spun ribbons were typically 2 - 3 mm wide and 20 - 40  $\mu\text{m}$  thick.

The phases of the ribbons were identified by X-ray diffraction (XRD) using  $\text{CuK}\alpha$  radiation in a Rigaku D/MAX2200PC diffractometer. The lattice parameters were evaluated by least-squares refinement from powder X-ray diffractograms. Thermomagnetic analysis (TMA) was performed in a magnetic balance in a field of 1 kOe. Magnetic properties of the ribbons were measured by a vibrating sample magnetometer (VSM) with a maximum applied field of 12 kOe. VSM was calibrated with a pure nickel flake. The microstructures of the specimens were examined by a scanning electron microscope (SEM).

## 3. Result and Discussion

Figure 1 shows the initial magnetization and room-temperature hysteresis curves of  $\text{Co}_{77}\text{Zr}_{18}\text{W}_5$  melt-spun ribbons produced at a wheel speed of 40 m/s. The hysteresis curve is very smooth and the remanence ratio

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(Mr/Ms) exceeds 0.6, reflecting that an exchange-coupling effect might have occurred in these ribbons. The inset shows the hysteresis curves of  $\text{Co}_{77}\text{Zr}_{18}\text{W}_5$  ingot as a function of applied magnetic field. We can see that the as-cast alloy nearly has no coercivity, suggesting that the process of quenching change the phase in the ribbons. For the  $\text{Co}_{77}\text{Zr}_{18}\text{W}_5$  melt-spun ribbons, it has the coercive value of 4.3 kOe, which is higher than that of Co-Zr-B melt-spun ribbons (3.6 kOe) [7]. On the other hand, the large slope of magnetization at 12 kOe indicates that the specimens are not saturated. Much larger field is required to completely saturate the coercivity.

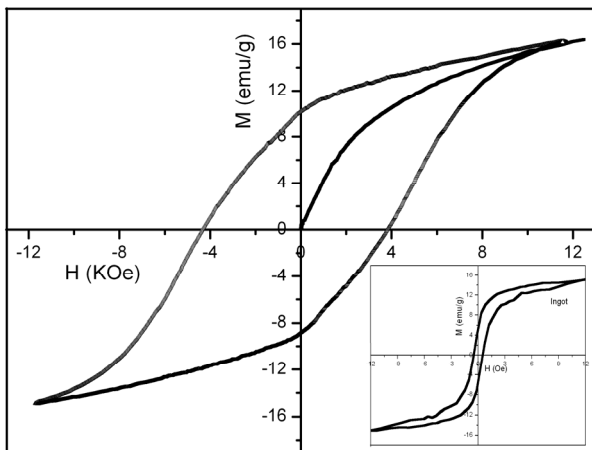
The magnetic properties of ingot and melt-spun ribbons are listed in **Table 1**. In the calculation of the maximum energy product  $(\text{BH})_{\text{max}}$ , the density of the melt-spun ribbons is assumed to be  $8.82 \text{ g/cm}^3$ . The maximum value of coercive field  $H_C$  were obtained under 12 kOe magnetic field. As can be seen, a much larger  $H_C$  and  $(\text{BH})_{\text{max}}$  improvement are obtained for the  $\text{Co}_{77}\text{Zr}_{18}\text{W}_5$  ribbons than the ingot. This value of coercivity is also much larger than the value of the undoped  $\text{Co}_{82}\text{Zr}_{18}$  melt-spun ribbons and annealed samples. It can be considered that the magnetic performance in polycrystalline Co-Zr alloys can be improved by the substitutions of W for Co. This improvement can be understood based on the dependence of the crystal structure and microstructure.

To understand the phases that exist in the studied ribbons, X-ray diffraction analysis was carried out. **Figure 2** shows the X-ray diffraction pattern of  $\text{Co}_{77}\text{Zr}_{18}\text{W}_5$

melt-spun ribbons. From the X-ray diffraction analysis, only a single  $\text{Co}_5\text{Zr}$  phase is found in the ribbons. The structure of the binary  $\text{Co}_5\text{Zr}$  phase is of fcc type having a  $F43m$  or  $F23$  space group with  $a = 0.67 \text{ nm}$ . It has been reported that the XRD patterns of  $\text{Co}_{82}\text{Zr}_{18}$  melt-spun ribbons (the surface velocity of 40 m/s) and of that annealed consist of  $\text{Co}_{11}\text{Zr}_2$ ,  $\text{Co}_2\text{Zr}$ , fcc-Co,  $\text{Co}_{23}\text{Zr}_6$  and  $\text{Co}_5\text{Zr}$  phase [5]. The XRD pattern suggests that W doping can decrease the amount of other phases. By least-squares refinement from powder X-ray diffractograms we get that the substitution of Co by the relatively larger atomic radius W leads to an increase of the  $\text{Co}_5\text{Zr}$  phase lattice constants of  $a = 0.6821 \text{ nm}$ . We also detected the XRD of  $\text{Co}_{77}\text{Zr}_{18}\text{W}_5$  ingot and almost no  $\text{Co}_5\text{Zr}$  phase was found. However, in the investigated  $\text{Co}_{77}\text{Zr}_{18}\text{W}_5$  melt-spun ribbons only the  $\text{Co}_5\text{Zr}$  phase is detected. This indicates that the W additive plays an important role in stabilizing  $\text{Co}_5\text{Zr}$  phase and W is an effective element to stabilize the metastable  $\text{Co}_5\text{Zr}$  phase.

**Figure 3** shows the thermomagnetic curve of  $\text{Co}_{77}\text{Zr}_{18}\text{W}_5$  melt-spun ribbons. We can see that the thermomagnetic curve exhibits a single magnetic transition near  $475^\circ\text{C}$ . It is clear that the  $\text{Co}_{77}\text{Zr}_{18}\text{W}_5$  melt-spun ribbons consist a single  $\text{Co}_5\text{Zr}$  phase. The Curie temperature  $475^\circ\text{C}$  is lower than that of the binary  $\text{Co}_5\text{Zr}$  phase ( $T_C = 500^\circ\text{C}$ ) in Co-Zr-B alloys [5]. Similar results have been observed in Co-Zr-B-Si alloys [8]. As far as we know, the decreasing of Curie temperature is possibly due to the increasing of lattice constants by the size effect, because of the change of the  $3d$  band structure resulting from the increasing of lattice constants [12]. Corresponding to the XRD studies above, the investigated specimens, consisting more  $\text{Co}_5\text{Zr}$  phase, exhibits a higher coercivity. These results lead to the conclusion that  $\text{Co}_5\text{Zr}$  phase is the hard magnetic phase in Co-Zr system alloys.

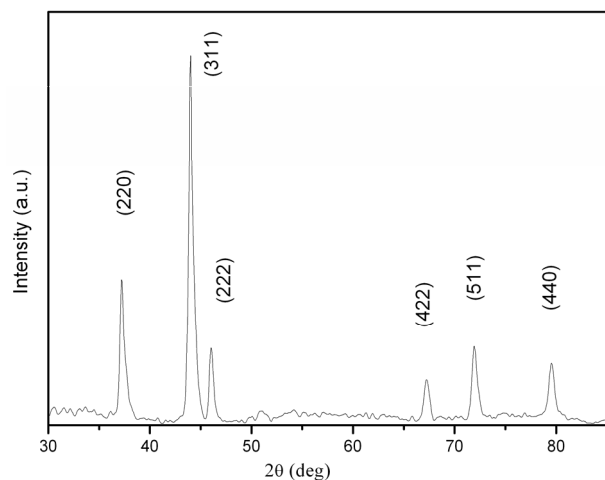
It is well known that annealing of rapidly solidified



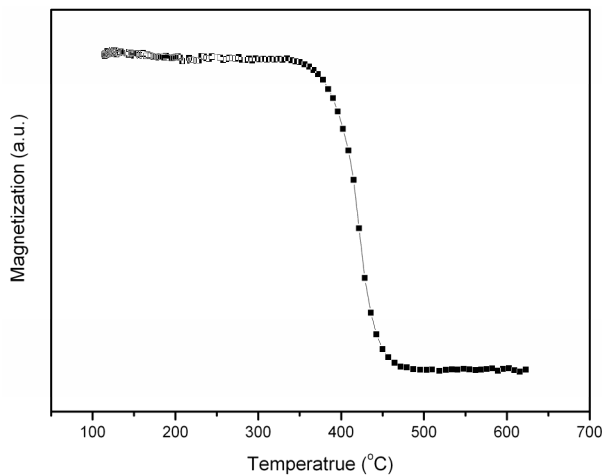
**Figure 1.** Initial magnetization and hysteresis curves of  $\text{Co}_{77}\text{Zr}_{18}\text{W}_5$  melt-spun ribbons.

**Table 1.** Magnetic properties of the As-cast  $\text{Co}_{77}\text{Zr}_{18}\text{W}_5$  ingot and melt-spun ribbons.

$\text{Co}_{77}\text{Zr}_{18}\text{W}_5$	$H_C$ (kOe)	$(\text{BH})_{\text{max}}$ (MGOe)	$\sigma_s$ (KGs)	$\sigma_r$ (KGs)	$\sigma_r/\sigma_s$
As-Cast	0.43	0.04	1.61	0.61	0.38
Melt-Spun	4.35	0.26	1.79	1.13	0.63



**Figure 2.** XRD pattern of  $\text{Co}_{77}\text{Zr}_{18}\text{W}_5$  melt-spun ribbons. The peaks can be indexed according to the  $\text{Co}_5\text{Zr}$  phase.

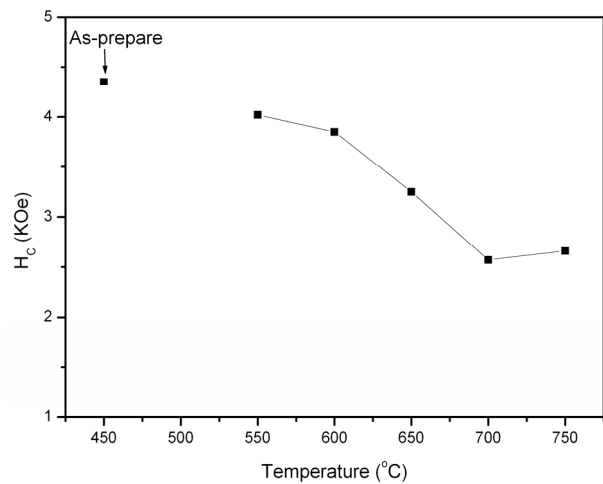


**Figure 3.** Thermomagnetic curve of  $\text{Co}_{77}\text{Zr}_{18}\text{W}_5$  melt-spun ribbons.

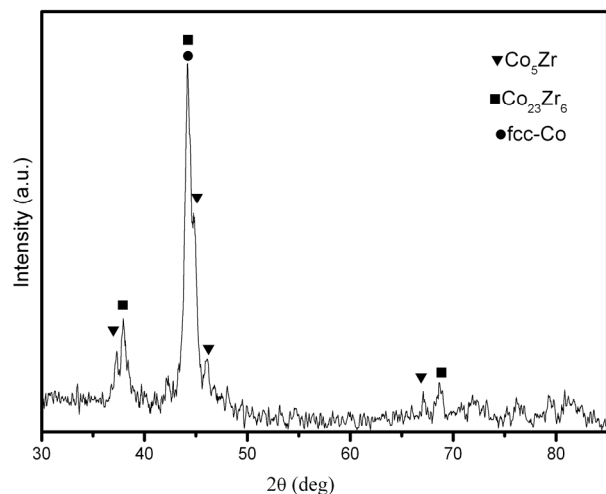
alloys results in the change in the grain size and the crystalline phase, which should give rise to the change in the magnetic properties. So the ribbons were annealed at temperatures between  $550^\circ\text{C}$  and  $750^\circ\text{C}$  for 20 min. **Figure 4** shows the dependence of coercivity of  $\text{Co}_{77}\text{Zr}_{18}\text{W}_5$  melt-spun ribbons on the annealing temperature. We can find that the coercivity of the annealed melt-spun ribbons decreases initially with increasing the annealing temperature from 4.0 kOe at  $550^\circ\text{C}$  to the minimum value 2.4 kOe at  $700^\circ\text{C}$ , then gradually increasing from 2.4 kOe at  $700^\circ\text{C}$  to 2.6 kOe at  $750^\circ\text{C}$ . Virtually, all the annealed specimens have a lower coercivity value than the as melt-spun ribbons. Heat treatment of the  $\text{Co}_{77}\text{Zr}_{18}\text{W}_5$  melt-spun ribbons results in a decrease of the coercivity, as was also found in Co-Zr-M ( $M = \text{Mo}, \text{C}, \text{Si}, \text{Al}$ ) melt-spun ribbons [3,13].

The corresponding XRD pattern of the  $\text{Co}_{77}\text{Zr}_{18}\text{W}_5$  ribbons annealed at  $700^\circ\text{C}$  is shown in **Figure 5**. Three phases, namely,  $\text{Co}_5\text{Zr}$ ,  $\text{Co}_{23}\text{Zr}_6$  and fcc Co phase, were found in the annealed  $\text{Co}_{77}\text{Zr}_{18}\text{W}_5$  ribbons. It is clear that the amount of  $\text{Co}_5\text{Zr}$  phase in the annealed  $\text{Co}_{77}\text{Zr}_{18}\text{W}_5$  ribbons is less than that of the as-prepared ribbons. Obviously no detection of  $\text{Co}_{11}\text{Zr}_2$  phase was found in both the as-prepared and annealed ribbons. This may be due to that the equilibrium  $\text{Co}_{11}\text{Zr}_2$  should be a soft magnetic phase in Co-Zr system as reported [5].

The microstructures of the  $\text{Co}_{77}\text{Zr}_{18}\text{W}_5$  ribbons of before heat treatment and the  $\text{Co}_{77}\text{Zr}_{18}\text{W}_5$  ribbons annealed at  $700^\circ\text{C}$  for 20 min were analyzed by SEM, as we can see in **Figure 6**. The grain size of  $\text{Co}_{77}\text{Zr}_{18}\text{W}_5$  melt-spun ribbons is too small to determine by SEM (less than  $0.1 \mu\text{m}$ ) and the ribbons annealed at  $700^\circ\text{C}$  for 20 min have fine grains (about  $2 \mu\text{m}$ ). This suggests that heat treatment of the  $\text{Co}_{77}\text{Zr}_{18}\text{W}_5$  melt-spun ribbons results in the dramatic change in the grain size. According to the micro-structural studies, the change of the coercivity for the



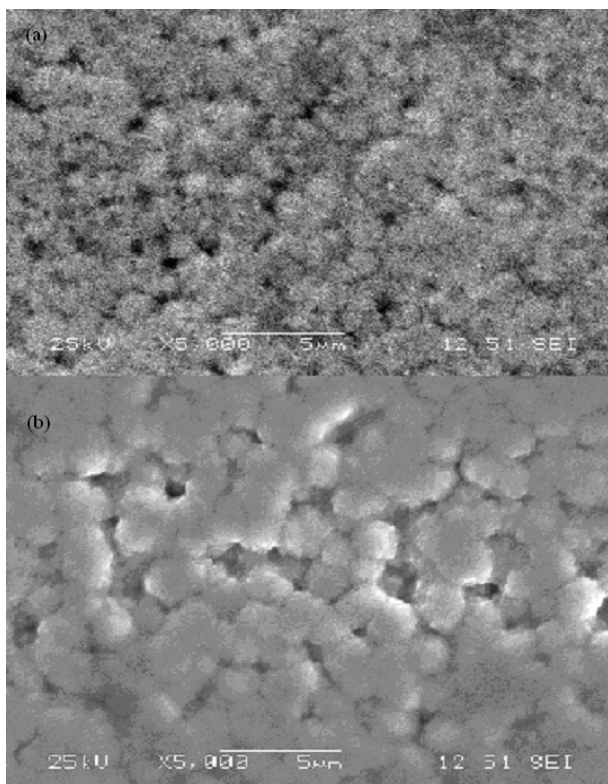
**Figure 4.** Dependence of coercivity of melt-spun ribbons on the annealing temperature from  $550^\circ\text{C}$  to  $750^\circ\text{C}$ .



**Figure 5.** XRD patterns of the  $\text{Co}_{77}\text{Zr}_{18}\text{W}_5$  melt-spun ribbons annealed at  $700^\circ\text{C}$ .

annealed specimens is considered to the change of the grain size of  $\text{Co}_5\text{Zr}$  phase, that is, the annealing temperature. The same results have been found in Co-Zr alloys [11]. On the other hand, compared with the as-prepared ribbons, we can see that the decrease of the coercivity for the annealed specimens is suggested to originate from the decreasing of the amount of  $\text{Co}_5\text{Zr}$  phase. These results further confirm that  $\text{Co}_5\text{Zr}$  phase is the hard magnetic phase in Co-Zr system alloys.

We also measured the coercivity of the minor hysteresis loops of  $\text{Co}_{77}\text{Zr}_{18}\text{W}_5$  ribbons in dependence with the applied magnetic field. It was found that the coercivity of the ribbons increases drastically at the low applied field until the external field exceeds the coercivity value, whereupon it reaches the maximum value. Moreover, the low-field susceptibility, determined by reversible displacement of the walls, is very large. Magnetic saturation is



**Figure 6.** SEM micrographs of  $\text{Co}_{77}\text{Zr}_{18}\text{W}_5$  melt-spun ribbons (a) and of the annealed at  $700^\circ\text{C}$  (b).

obtained in comparatively low applied field. These behaviors indicate that the coercivity of the studied  $\text{Co}_{77}\text{Zr}_{18}\text{W}_5$  ribbons is mainly governed by the nucleation of the reversed domain [6,14]. The physical mechanism should be complex and detailed work for that is required in the future.

#### 4. Conclusion

In conclusion a single metastable  $\text{Co}_5\text{Zr}$  phase is obtained in the  $\text{Co}_{77}\text{Zr}_{18}\text{W}_5$  melt-spun ribbons. The high coercivity of 4.3 kOe is proved coming from the hard magnetic phase of  $\text{Co}_5\text{Zr}$ . Substitution of Co by the relatively larger atomic radius W can lead to an increase of the  $\text{Co}_5\text{Zr}$  phase lattice constants and exhibit a Curie temperature of about  $475^\circ\text{C}$ . The coercivity of the annealed specimens decreases than the as-prepared ribbons because of the decrease of hard magnetic phase and the change of grain size. The excellent hard magnetic properties may make the Co-Zr alloys become very attractive candidate materials for permanent magnetic applications. The related physics is complex and require a further fundamental investigation.

#### 5. Acknowledgements

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