Journal of Alloys and Compounds 644 (2015) 7–12

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: www.elsevier.com/locate/jalcom

Microstructure and magnetic properties in as-cast and melt spun Co–Zr alloys

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ARTICLE INFO

Article history:
Received 23 January 2015
Received in revised form 15 April 2015
Accepted 17 April 2015
Available online 30 April 2015

Keywords:
Co–Zr alloys
Melt-spinning
Microstructure
Magnetic properties

ABSTRACT

The microstructure formation during solidification of as-cast and melt-spun Co-rich (Co–13 at.%, 16 at.% and 18 at.% Zr) Co–Zr alloys was studied. The microstructure evolution significantly differs during melt spinning owing to high cooling rate, although the volume fraction of α-Co was found to decrease with increasing Zr content in both as-cast and melt-spun alloys. The magnetization values decreased and the coercivity increased with increase in Zr content in both as-cast and melt-spun alloys. However, the melt-spun alloys showed a significantly higher coercivity which can be attributed to the finer scale of microstructure achieved due to the higher cooling rate.

1. Introduction

The search for materials for renewable energy applications has become one of the thrust areas of material research in recent years [1–4]. Permanent magnets which find applications in wind turbine generators and energy harvesting devices are one of the key materials to produce energy in a cheaper and greener way. Among the permanent magnets, rare earth permanent magnets qualify as the best in the class owing to their high magnetocrystalline anisotropy, large coercivity and high energy product [5–11]. However, there is an increasing concern over the waning supply of rare earth metals and their high cost. This has driven an intensive search for rare earth free permanent magnets in recent times.

Several researchers [12–15] have investigated Fe–Pt and Mn based alloys such as Mn–Bi, Mn–Al, and Mn–Al–C as viable rare earth free alternatives to the traditional rare earth permanent magnets. The concern regarding Fe–Pt alloys is the extremely high cost of Pt which restricts its use in several commercial applications. However, studies are still underway for improving the magnetic properties of Mn based alloys albeit their energy product is much less than rare earth permanent magnets.

In recent times, Co-rich Co–Zr alloys have drawn attention of researchers [16,17] as a feasible permanent magnet that is devoid of rare earths. In this alloy system, the phase of choice is the Zr_2Co_{11} phase owing to its high Curie temperature and non-cubic crystal symmetry which leads to high anisotropy. Initial studies exploring the possibility of making permanent magnets with Co–Zr alloys using melt spinning and cluster deposition methods for producing the material with extremely fine microstructural length scale have been reported in literature [16,17]. These initial studies reveal a strong promise for these alloys for qualifying as a permanent magnet and demonstrate the importance of processing them under non-equilibrium conditions such as high cooling rates. However, an insight into the microstructure formation during non-equilibrium processing and how it affects magnetic properties is still evasive. Further, the phase diagram of Co–Zr system (Fig. 1) indicates that in the region of interest (10–25 at.% Zr) two peritectic transformations at 1331 & 1272 °C and one eutectic transformation at 1254 °C involving two intermetallic phases Zr_2Co_{11} and Zr_6Co_{23} [18], may result in the formation of complex microstructural features under non-equilibrium cooling conditions. The intrinsic understanding of development of such complex microstructure under high cooling rate is extremely important in Co–Zr system as the magnetic properties are intimately related to the microstructural attributes. Therefore, the present study has been taken up to establish the mechanism of formation of microstructure in Co-rich Co–Zr alloys in as-cast condition as well as after melt-spinning where the cooling rates are high. The effect of microstructural attributes thus formed on the magnetic properties has also been discussed.

2. Experimental

The Co–x at.% Zr (x = 13, 16, 18) alloys were prepared under argon atmosphere by vacuum arc melting of high purity (>99.5%) Co and Zr taken in appropriate quantities. In order to ensure the homogeneity of the alloy the buttons were re-melted at

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http://dx.doi.org/10.1016/j.jallcom.2015.04.156
0925-8388/

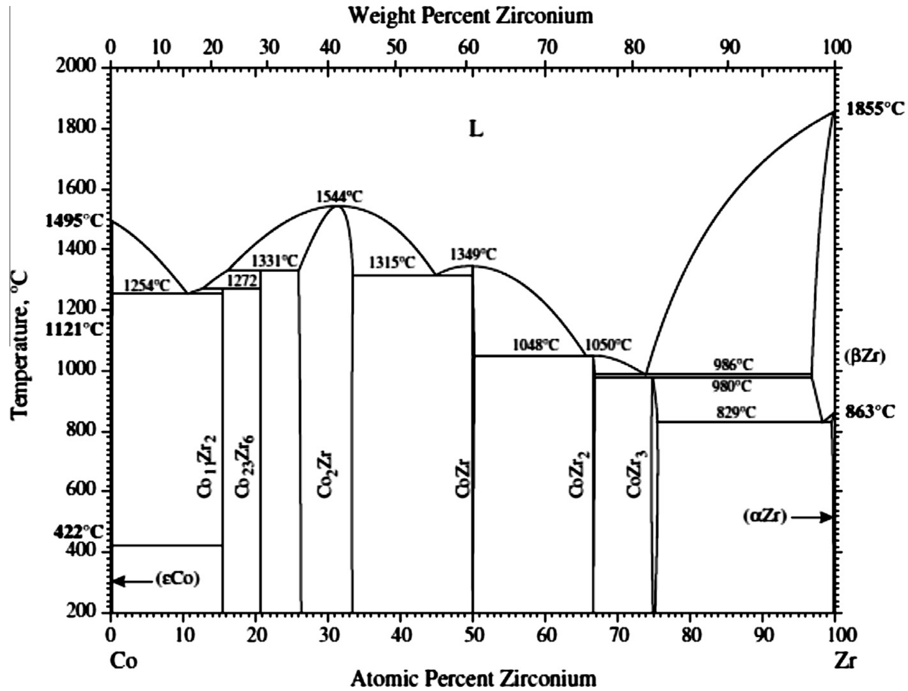

Fig. 1. Phase diagram of Co–Zr [18].

least five times. The chemical compositions of the arc melted buttons were determined using inductively coupled plasma-optical emission spectroscopy (ICP-OES) and found to be close to the nominal composition. The alloys were subsequently melt-spun using a single roller melt spinning unit under argon atmosphere. During melt spinning the alloys were taken in a quartz tube with an open slit at the bottom and melted using an induction coil. The ribbons were produced by allowing the liquid melt to fall on a water cooled copper wheel rotating at speed of 47 m/s. The microstructure of the alloys was investigated using high resolution field emission scanning electron microscope (make M/s Zeiss) with Oxford EDS detector. The magnetic properties of the alloys were characterized using SQUID VSM (M/s Quantum Design, USA) up to a magnetic field of 40 kOe.

3. Results and discussions

3.1. Microstructure of as-cast alloys

The back scattered electron images of the as-cast Co–x at.% Zr (x = 13, 16, 18) are shown in Fig. 2. The microstructure of the 13 at.% Zr alloy in the as-cast condition exhibits presence of two phases (Fig. 2a). The micro-chemical analysis of these phases reveals that the composition of the bright phase corresponds to γ (Orthorhombic) [19,20] phase (also termed in literature as Zr_2Co_{11}) in the Co–Zr binary phase diagram (Fig. 1). As the phase diagram (Fig. 1) indicates the intermetallic phases have no solid solubility range, therefore the phases could be identified based on micro-chemical analysis. The phase with darker contrast is a eutectic mixture of α-Co (FCC, SG: Fm-3m) and γ phase, oriented in regular lamellar microstructure as observed from the magnified view of this phase shown in inset of Fig. 2a. The volume fraction of the phases was calculated using Image Tool™ software and enumerated in Table 1. The volume fraction of the eutectic phase and γ phase are found to be nearly same. The microstructural observations led to a comprehensive understanding on the solidification sequence and how the observed microstructure is formed and is described in Table 2.

The microstructure of 16 at.% Zr alloy in the as-cast condition as shown in Fig. 2b depicts the presence of a dark phase, which is an eutectic mixture of α-Co and γ phases similar to that observed in the 13 at.% Zr alloy. The volume fraction of the eutectic phase, however, is found to decrease in this sample (Table 1). Two other phases with slightly differing atomic number contrast are also present in the microstructure, which are termed hereafter as bright and grey phases. The secondary electron image obtained on an etched sample, however, reveals a clear contrast between these two phases as shown in inset of Fig. 2b. The micro-chemical analysis of these phases, reveals that the bright and the grey phases are δ [Cubic, SG: Fm-3m] (also known as Zr_6Co_{23}) and γ phases respectively, in the Co–Zr phase diagram. Since the average atomic number of γ is 20.5, whereas that of δ phase is 25, the difference in contrast obtained in the BSE image is extremely feeble. The morphology of the δ–γ interface, especially the presence of re-entrant corners (*indicated by white arrows in* Fig. 2b) suggests that the γ phase forms by a peritectic transformation of $L + \delta \rightarrow \gamma$. The transformation is however incomplete and as a result the un-reacted δ is found in the microstructure (Table 2). The eutectic phase is formed from the last solidified liquid with regular lamellar morphology of γ and α-Co phases. The γ phase thus formed as a part of eutectic lamellae is different from the primary γ that forms during the peritectic transformation (Table 2).

The microstructure of Co–18 at.% Zr alloy in the as-cast condition is shown in Fig. 2c. The microstructure shows a two phase contrast wherein the dark phase corresponds to γ, whereas the bright phase corresponds to δ. The morphologies of these phases indicate that the γ phase forms by the peritectic reaction between liquid and δ as in the case of Co–16 at.% Zr alloy. In this case however, no eutectic formation is noticed as the composition is situated towards right side of the γ phase line in Zr–Co phase diagram. The volume fraction of these two phases were measured (Table 1) and it is found that ~32% of pro-peritectic residual δ phase is observed in the microstructure. The large volume fraction of un-reacted δ phase indicates that the peritectic reaction remains largely incomplete in this case.

3.2. Microstructure of melt spun ribbons

The high resolution scanning electron micrograph of melt-spun Co–13 at.% Zr alloy is shown in Fig. 3a. The micrograph depicts extremely fine grains of average size of about 150 nm. The grain boundaries are decorated with very thin layer of primary γ-phase.