

**PREPARATION OF RARE EARTH - TRANSITION METAL (RE: Y,
TM: CO) INTERMETALLIC COMPOUNDS
BY CALCIOTHERMIC REDUCTION DIFFUSION PROCESS**

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Abstract

Rare earth cobalt alloys have many special magnetic properties and can be used to prepare magnetic and magneto-optical components. The yttrium – cobalt intermetallic compounds are prepared by calciothermic reduction – diffusion (CRD) process at temperature of 1000°C, under argon atmosphere. Yttrium oxide, metallic cobalt powder, metallic calcium are used as raw materials in this process. Calcium acts as the reductant, which is used to prepare the YCo₅ magnetic material. XRD, SEM, EDAX and some thermodynamic valuation have been carried out on the products. The chemical reactions controlled by unreacted core model theory were studied.

Keywords: Calciothermic reduction process (CRD), Intermetallics, Rare earth Cobalt alloys, Gibbs free energy

Introduction

Permanent magnetic materials have revolutionized technology; and are of growing interest to the electronics industry and to manufacturers of electro-mechanical devices, with applications in many electronic apparatus, circuits, electric motors, consumer, and defence products. These magnets have major influence on the size, efficiency, stability, and cost of cited devices. The rare earth alloy magnets that have been most extensively studied and developed are SmCo and NdFeB. There are three families of rare earth magnets commercially available, namely SmCo₅, Sm₂Co₁₇ and Nd₂Fe₁₄B based magnets, which were developed in the 1960s, 1970s and 1980s, respectively [1]. In recent years, a new generation of lanthanide-based intermetallic materials have emerged, with excellent magnetic properties and also primary interest is

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focused on the light lanthanides, i.e. La, Ce, Pr, Nd, Sm and Y, even though the light lanthanides generally have smaller magnetic moments than the heavy lanthanides. In the LnCo_5 structure, the heavy lanthanide moment couples antiferromagnetically with the cobalt moment, reducing the saturation magnetization.

There are four major possible routes for the production of rare earth–cobalt alloys. These are (1) arc melting, (2) induction melting, (3) electro-winning, and (4) reduction-diffusion process. Amongst these, the first two methods are well established and widely practiced. These methods are simple to operate and yield alloys of the highest purity. However, both these processes require the alloy constituents in their elemental form/s, and hence turn out to be quite expensive [2]. The reduction-diffusion (RD) process is a method by which the rare earth-transition metal intermetallic compound powders can be prepared over a relatively wide temperature range using the cheap rare earth oxides, transition metal powder and calcium (or CaH_2) as the raw materials. In many cases, calcium hydride (CaH_2) has been used as reducing agent [2].

The advantages of the reduction-diffusion (RD) method are the direct use of rare earth oxides as raw materials, low cost, and elimination of the homogenization process for the elimination α -Fe phase in the ingot. The RD process is relatively less capital intensive, easy to operate and straightaway yields alloys of the desired composition [3]. Therefore, the RD process is a promising technique, with low cost for the preparation of magnetic materials. In the present study, the proposed Y-Co alloy has been produced using the calciothermic reduction-diffusion process.

Experimental Procedure

The raw materials used in experiments are powders of yttrium oxide (Y_2O_3), metallic cobalt powder and calcium granules with purity of 99.55% in mass content as stoichiometric ratio. These powders were mixed and pressed into pellets, at pressure of 1.44 tons / cm^2 . The pellet was then placed in a high density alumina crucible, which was placed in high temperature electrical furnace at 1000 °C for 7 hours, under argon atmosphere. After the reaction, the product was cooled to room temperature and the sample was taken from the crucible and then washed with 5% dilute acetic acid and distilled water subsequently, to remove the impurities and CaO. The desired YCo_5 powder was weighed to calculate the rate of reduction – diffusion, also called as a “conversion rate” (α) [4].

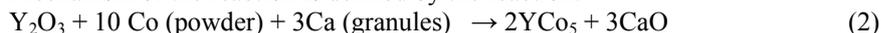
Rate of reduction-diffusion may be expressed as:

$$(\alpha) = M_Y / M_Y^\circ \times 100\% \quad (1)$$

where M_Y is the weight of Y in YCo_5 formed by the diffusion of Y into Co, and M_Y° is the weight of Y in the raw materials [3].

Mechanism of reaction

Mechanism of the reaction is defined by the reaction:



From the above equation, it is understood that Y_2O_3 can be reduced by Ca, and then Y diffuses in the matrix of Co forming YCo_5 . The process consists of two steps:

(1) Under the elevated temperature, Ca vapour quickly diffuses to the surface of Y_2O_3 , where Y_2O_3 is reduced by Ca; and Y is produced.

(2) The Y produced diffuses to the adjacent surface of Co powder to form YCo₅.

The reaction continues from the exterior to the interior, so it can be controlled by unreacted core model theory. The formula is derived from the relationship between conversion rate and time.

If the reaction is controlled by gas phase transferring reaction [3], then:

$$kt = \alpha \quad (3)$$

In the case if the reaction is controlled by gas-solid interface chemical reaction [3], then:

$$kt = 1 - (1 - \alpha)^{1/3} \quad (4)$$

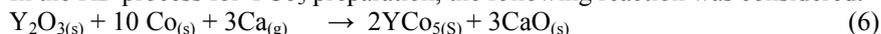
If the reaction is controlled by resultant layer internal diffusion [3], then the following equation may be applied:

$$kt = 1 - 3(1 - \alpha)^{2/3} + 2(1 - \alpha) \quad (5)$$

where, α - conversion rate, t - reaction time, k - reaction rate constant. Using Eq. (5), we obtained the rate constant for internal diffusion of this system as $8.25 \times 10^{-7} \text{ sec}^{-1}$.

Thermodynamic Aspects

In the RD process for YCo₅ preparation, the following reaction was considered:



Assuming, the YCo₅ is an ideal solution, the change in Gibbs free energy due to formation of a solution of mixing [5] is given by:

$$\Delta G_{298}^M = RT (X_A \ln a_A + X_B \ln a_B) \quad (7)$$

For an ideal solution, $a_A = X_A$



Rearranging the equations (8), (9) and (10), the Gibbs free energy of mixing of solution at 1273 K was calculated. The change in Gibbs free energy due to formation of a solution at 1273 K is found to be -568.971 KJ / mole.

Characterization

X-ray powder diffraction (XRD) patterns were recorded with a PW3040/60 X'pert PRPANalytical, Netherlands diffractometer with Cu K α radiation. The morphology was examined with a scanning electron microscope (SEM) Hitachi. Chemical composition of the samples was examined by energy dispersive-X-ray analyzer (EDAX).

Results and Discussion

XRD Analysis

The XRD patterns were obtained for the specimens produced by reaction at 1273K for 7 hours. The well defined peaks of YCo_5 and CaO and other impurities observed in this system are shown in Figure 1.

The average crystalline size of samples was calculated according to the following equation:

$$T = k * \lambda / B * \cos \theta_B \quad (11)$$

where, T= average crystalline size of the samples, K= constant dependent on crystallite shape (0.89), Λ =X-ray wave length (1.54 nm), B= FWHM (full width at half max), and θ_B = Bragg angle respectively.

The full-width at half-maximum (FWHM) of the YCo_5 peak was used in the Scherrer equation (11) to independently estimate the average crystalline size of YCo_5 , ranging from 0.1 μm to 0.6 μm .

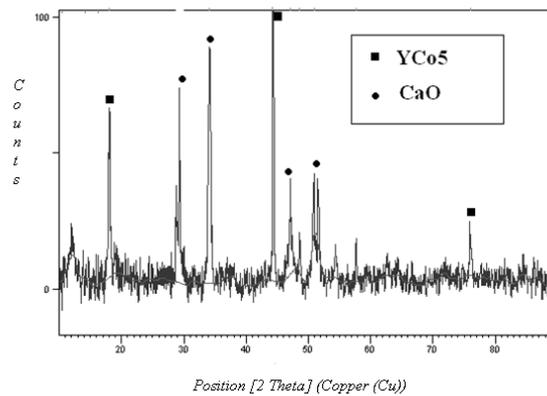


Figure 1. XRD peaks of YCo_5 produced at 1000 °C

SEM Analysis

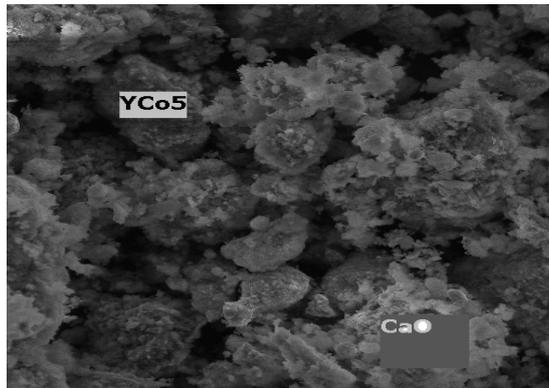


Figure 2. (SEM). Morphology of YCo_5 produced at 1000 °C

SEM micrographs revealing the particle size and morphology of the prepared crystals are shown in Figure 2. The YCo_5 grains in the pellets were examined after the calciothermic reduction-diffusion process. The rare-earth – intermetallic products (YCo_5) were found to be hexagonal in shape. The morphology of YCo_5 and minor impurity (CaO) was examined. The YCo_5 particle size analysis has been carried out at 20 μm standard size.

EDAX analysis

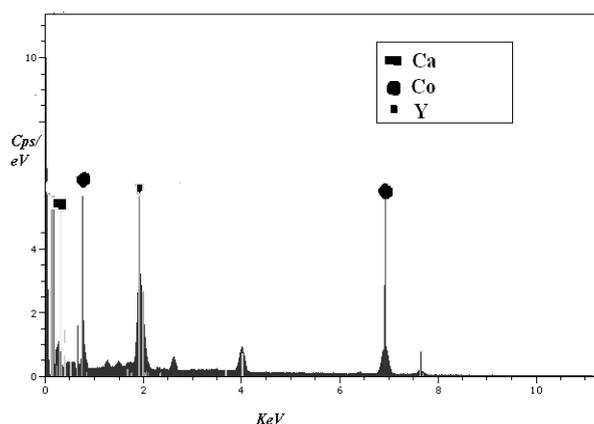


Figure 3. EDAX of YCo_5 at produced at 1000 °C

Chemical composition has been observed by EDAX technique after calciothermic reduction-diffusion process and presented in Figure 3. The result analyzed with EDAX shows that the atomic percentage-wise composition of YCo_5 was Y=15.0 and Co = 75%, respectively.

Conclusions

In Ca- Y_2O_3 –Co system, it is possible to produce YCo_5 alloy by reduction-diffusion process. The reduction process can be described by contracting core model. The rate constant is $8.25 \times 10^{-7} \text{ sec}^{-1}$ (for 7 hours) was required for the conversion of reactants into the products. The Gibbs free energy of mixing of solution at 1273 K is -568.971 KJ/mol required to reduce the yttria and diffuses through the Co layer to form a YCo_5 . The EDAX analysis shows that the atomic percentage of YCo_5 were Y=15.0 and Co = 75%, respectively. The SEM image shows that the morphological and features of the synthesizing crystal and particle size is in the range of 20 μm . From the XRD results, the presence of pure YCo_5 alloy can be ascertained, along with minor impurity like CaO in the system. The reaction goes on from exterior to interior, so it can be observed by unreacted core model theory.

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