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MECHANISM AND SYNTHESIS OF YTTRIUM IRON (Y-Fe) ALLOY BY LOW TEMPERATURE PROCESS USING CALCIUM AS REDUCTANT

In this paper, study the preparation of Y-Fe alloy by reduction-diffusion process, which is novel technique for producing an alloy from its ores directly at different temperatures. From this work, investigates the particles size and morphology structure of alloy by X-Ray Diffraction (XRD), Energy dispersive-X-ray analyzer (EDAX) and Scanning Electron Microscope (SEM) respectively. Here study the thermodynamics of property of system such as Gibbs free energy and reaction kinetics of system respectively. The Vibrating Sample magnetometer (VSM) is used to study the magnetic properties of alloy such as cocerviety, saturation magnetization and retentivity.

Keywords: Gibbs free energy, Reaction kinetics, VSM, XRD, SEM

1. Introduction

Permanent magnets based on the lanthanides, Sm-Co and Nd-Fe-B, are exciting additions to the family of magnetic materials, from many perspectives. To the materials scientist, they are a new generation of lanthanide-based intermetallic materials, with excellent magnetic properties. To the electrical engineer, they are powerful components in designing new devices with greatly enhanced performance. To the magnet producer, they are new permanent magnet materials, with improved magnetic properties and several processing options. The first $SmCo_5$ magnets appeared in the late 1960's and early 1970's, due to the research and development efforts of several organizations, most notably: General Electric, Raytheon, Bell Telephone Laboratories, Wright Patterson Air Force Base, N.V. Philips and Brown Boveri et Cie. [1]. The Y-Co alloy system has been studied and reported earlier [2]. 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 (4) reduction-diffusion process. Of 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, and hence are very expensive. [3]

In most cases the calcium Hydride (CaH_2) was used as reducing agent. The calcium grain, which is cheaper than calcium hydride, was seldom used as reducing agent. Comparing with the conventional mixing and melting process, the RD process is promising one which has the advantages of simple, low cost and shorted producing period [4].

In the present study, we systematically investigated the effect of the magnetic properties of Y based alloy produced by the reduction-diffusion process.

The advantages of the Reduction-diffusion (RD) method are characterized by direct use of rare earth oxides as raw materials, low cost, and an omission of the homogination process for the elimination α-Fe phase in the ingot. The process is less capital intensive and easy to operate and straightway yields alloys of the desired composition.

2. Materials and methods

Yttrium oxide (Y_2O_3), metallic Iron powder and Calcium granules are taken in stoichiometric proportions. These powders are mixed roughly and then ground with mortar for 15 minutes. These mixtures are made into the pellets of dimensions of 30 mm diameter and 10 mm length, using hydraulic press, with applied as load of 1.44 tonne / cm^2. The pellet is kept in the high density alumina crucible having dimensions of 50 mm diameter and 70 mm length. The crucible is kept in the high temperature furnace at different temperature of 1223, 1273, 1323 K, under argon pressure, for 7 hours. Afterwards, the pellets are taken from the furnace, washed with 5% acetic acid and subsequently with distilled water. The CaO is removed by the washed with distilled water, then the useful product is taken, for detailed analysis.

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3. Characterization

X-ray powder diffraction patterns were recorded with a PW3040/60 X'pert PR PANalytical, Netherlands diffractometer with Cu K_a radiation. The morphology was examined with an instrument of Hitachi, Japan scanning electron microscope. Chemical composition of the samples was examined by Energy dispersive-X-ray analyzer. Magnetic properties are examined by VSM Model: 7404.

4. Thermodynamics of the system

The Y-Fe binary system has been studied extensively. Even though, there is no data of formation free energy of Y-Fe which could be used. All thermodynamics data are collected as reference [6].

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

$$Y_2O_3(s) + 3\,Ca(g) + 4\,Fe(s) = 3CaO(s) + 2YFe_2(s) \quad (1)$$

According to the Hess law of heat summation, equation (1) can be written as

$$Y(s) + 2Fe(s) = YFe_2 \quad (2)$$

$$Y_2O_3(s) + 3Ca(l) = 2Y(s) + 3\,CaO(s) \quad (3)$$

$$Ca_{(1)} = Ca(g) \quad (4)$$

Assuming (4), the YFe_2 is an ideal solution, the entropy change of YFe_2 formation at 298 K could be written as

$$\Delta S^{o}_{298} = -R(X_A \ln a_A + X_B \ln a_B) \quad (5)$$

From equation (2),

$$\Delta S^{o}_{298} = 5.3217 \text{ J / deg / mole} \quad (6)$$

Assuming that the thermal heat capacity of YFe_2 obeys the Newmann-Kopp's rule, the ΔCp of equation (2) is zero and the enthalpy change of equation (2) at 298 K becomes.

The formation free energy of YFe_2 could be obtained from equation (2)

$$\Delta G^{o}_{298(2)} = 22856.6 - 5.3217\,T \quad (7)$$

Using given data, equation (3),

$$\Delta S^{o}_{298(3)} = \{2S^{o}_{Y} + 3^{o}\,CaO\} - \{S^{o}_{Y2O3}\} \quad (8)$$

$$\Delta S^{o}_{298(3)} = 104.02\ JK^{-1}mol^{-1} \quad (9)$$

The enthalpy change of formation at 298 K in equation (3),

$$\Delta H^{o}_{298} = (\Delta H^{o}_{products} - \Delta H^{o}_{reactants}) \quad (10)$$

$$\Delta H^{o}_{298} = -269450 \text{ J / mole} \quad (11)$$

The Gibbs energy formation of equation (3) at 298 K is,

$$\Delta G^{o}_{298(3)} = -269450 - 104.02\,T \quad (12)$$

From equation (4), the Gibbs energy formation at 298 K can be written as,

$$\Delta G^{o}_{298(4)} = 117800 - 154.9\,T \quad (13)$$

Rearranging the equations (7), (12) and (13), the Gibbs energy formation of a reaction at 298 K is

$$\Delta G^{o}_{298(1)} = -105936.8 - 269.563\,T \quad (14)$$

The free energy change of reaction at 1223 K, 1273 K and 1323 K could be calculated as [4],

$$\Delta G = \Delta G^{o}_{298(1)} + RT \ln K \quad (15)$$

$$\Delta G_T = 105936.8 - 269.563\,T + RT \ln (P_{ca} / P^{o})^{-3} \quad (16)$$

Where the P_{ca} is the vapour pressure of calcium and P^{o} is the standard atmospheric pressure (101325 Pa).

$$\log P_{ca} = -8.92 \times 10^{3}\,T^{-1} - 139 \log T + 11.58 \text{ kPa [5]} \quad (17)$$

The value of ΔG at 1223 K, 1273 K, and 1323 K are –368.276 KJ / mole, –379 KJ / mole, –389.726 KJ / mole respectively.

5. Mechanism of reaction

The chemical reaction can be analyzed by the equation (1) [5]. In Ca-Y_2O_3-Fe reaction system, Y_2O_3 can be reduced by Ca and then Y which finally react with Fe, and forms YFe_2. The process of equation (1) consists of two steps: Under reaction temperature Ca vapour quickly diffuses to the surface of Y_2O_3 granules in porous specimen, where Y_2O_3 is reduced by Ca and then fresh Y is produced. The Y produced diffuses to the adjacent surface of Fe powder, where Y reacts with Fe to form YFe_2 and its nucleus grows at the interface, then the YFe_2 layer is formed gradually. The mode of Y vapour diffusing is by gas phase. There are two ways for Y to transfer on the surface of Fe powder. The reaction continues from the exterior to interior, so it can be described by unreacted-core model theory. The equation derived from the model was used to express the relation between conversion rate and time,

$$kt = 1 - 3(1 - \alpha)^{2/3} + 2(1 - \alpha) \quad (18)$$

Conversion rate (α) can be calculated by this equation

$$\text{Conversion rate or rate of Reduction-Diffusion } (\alpha) = M_Y / M^{\circ}_Y \times 100\% \quad (19)$$

where M_Y is the weight of Y in YFe_2 formed by the diffusion of Y into Fe and M°_Y is the weight of Y in the raw materials.

The value of $\alpha = 0.48$ at 1223 K

$$k = 1 - 3(1 - 0.0.48)^{0.66} + 2(1 - 0.48) / t$$

$$k_1 = 3.650 \times 10^{-6}\ sec^{-1} \quad (20)$$

The Value of $\alpha = 0.51$ at 1273 K

$$k_2 = 4.226 \times 10^{-6}\ sec^{-1} \quad (21)$$

The value of α = 0.53 at 1323 K

$$k_3 = 4.656 \times 10^{-6}\ sec^{-1} \quad (22)$$

6. Results and discussion

6.1. XRD Analysis

The XRD patterns for the specimens at 1273K for 7 hours. Fig. 1 shows that high peaks of YFe_2 and CaO and other impurities are observed in this system.

$$T = k * \lambda / B * \cos\theta_B \quad (23)$$

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), θ_B = Bragg angle respectively.However, the YFe_2 phase is found in the XRD pattern. The corresponding XRD peaks are coincided with the standard patterns of JCPDS data. It reveals that the presence of YFe alloy phase. The hkl values (3 1 1) for 100% intensity of the synthesized compound closely matched with the standard pattern (JCPDS 03-065-0113) for Y-Fe respectively. The full-width at half-maximum (FWHM) of the YFe peak was used in the Scherrer equation (23) to independently estimate the average grain size of ranging from 0.1 µm-0.46 µm.

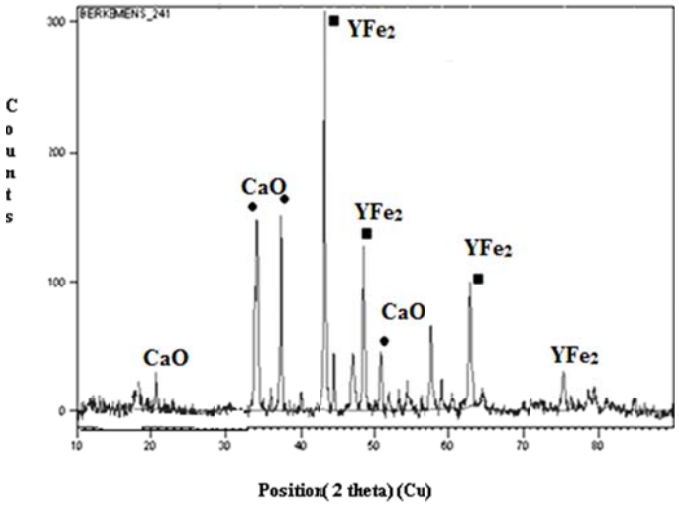

Fig. 1. XRD of Y-Fe system produced at 1273 K

6.2. SEM Analysis

Fig. 2 shows the scanning electron micrographs for the YFe_2 alloy powders obtained by RD process at 1273 K. The SEM micrographs have shown assorted crystal features with non-uniform particle morphology. The powders are crystalline in nature with finer grain size. At higher magnifications, the picture reveals the fact that the particles are dissociated with each other exhibiting in cubical shape. The average particle size is found to be between 2-10 µm.

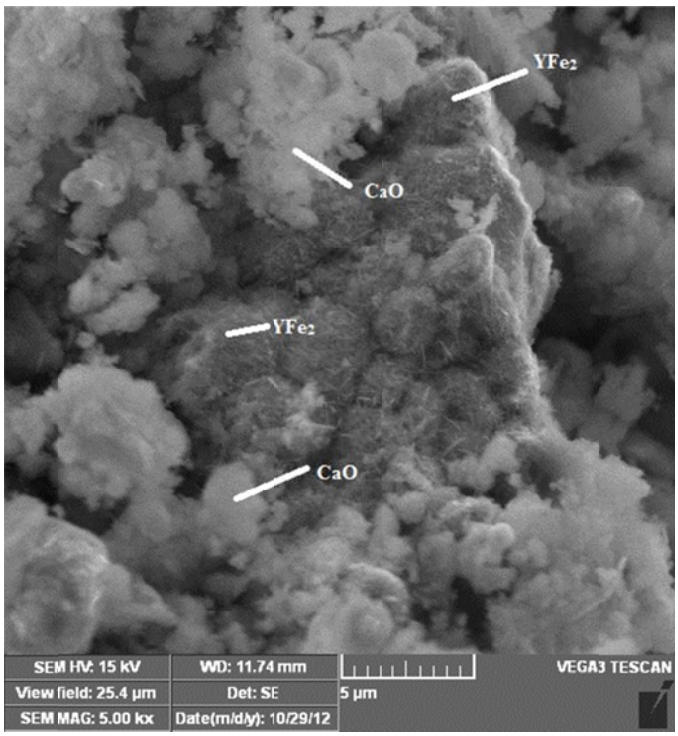

Fig. 2. (SEM) Morphology of Y-Fe system produced at 1273 K

6.3. EDAX analysis

Fig. 3 shows chemical compositions have been observed by EDAX technique after calciothermic reduction-diffusion process. The result analyzed with EDAX shows that the atomic percentage of YFe_2 and CaO were Y = 25.0%, Fe = 65%, and remaining some traces of Ca and O percentage in this system.

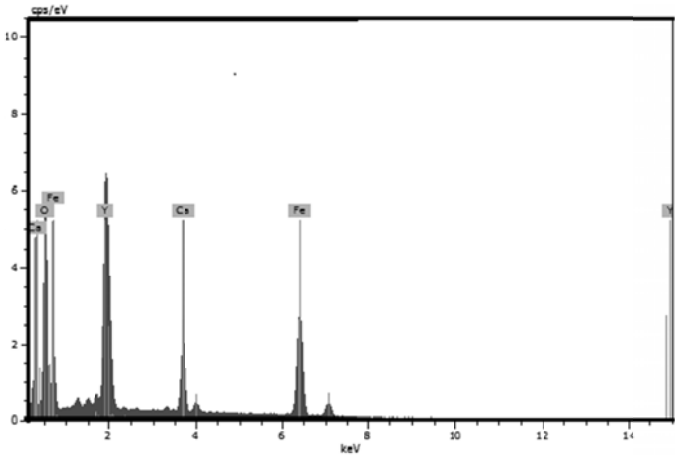

Fig. 3. Schematic diagram of EDAX Result of YFe_2 at 1273 K

6.4. Vibrating Sample Magnetometer

From Fig. 4, hysteresis loop described that the magnetization value is 23.132 emu/g under plot between the magnetic field (G) and moment/mass (emu/g) (B). The magnetic curve starts from zero with increasing magnetic field (G) and also moment/

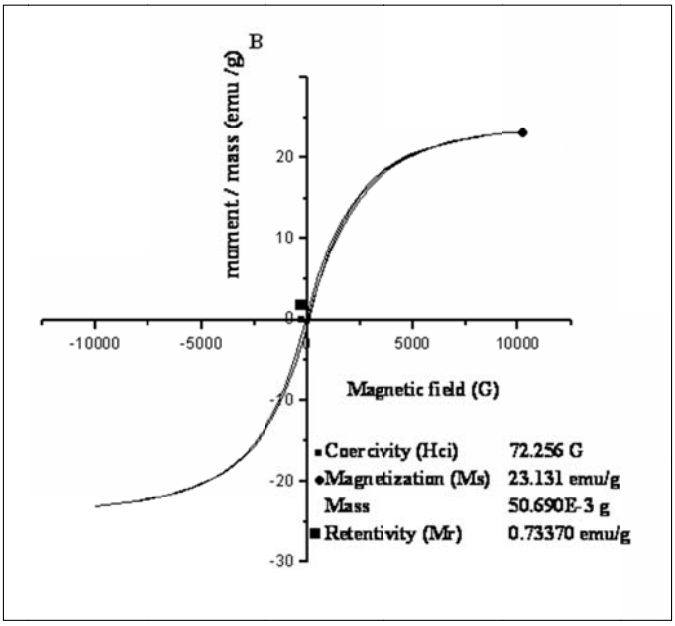

Fig. 4. (VSM) Hystersis loop of Y-Fe system produced at 1273 K

mass B (emu/g). If the magnetization curve after saturation, with applied magnetic field in opposite direction to that of the original moment/mass (emu /g) is known as coercivity. The coercivity value is 72.256 G (72.256 × 10^{-4} T). It reveals soft magnetic material must have initial permeability and a low coercivity with a relatively low applied field (i.e easily magnetized and demagnetized) and still has low hysteresis energy losses. The retentivity is used for remanence measured in units of magnetic flux density. In other words, it is the ability of a material to retain a certain amount of residual magnetic field when the magnetizing force is removed after achieving saturation. The retentivity value is 0.73370 emu /g.

7. Conclusion

Calciothermic Reduction Diffusion process is used to novel techniques used to prepare pure and Intermetallic compounds. The rate constant could be calculated by unreacted core model theory. The Gibbs free energy of formation of solution at 1223 K, 1273 K, and 1323 K are –368.276 KJ / mole, –379 KJ / mole, –389.726 KJ / mole respectively, to produce the product YFe_2 (mole). The result analyzed in the EDX shows that the atomic percentages of Y and Fe in YFe_2 were Y = 15%, Fe = 65%, and remaining some traces of Ca and O percentage in this system. respectively. The SEM image reveals that the YFe_2 alloy particles are non-uniform in size and shape. At higher magnifications, the picture reveals the fact that the particles are dissociated with each other exhibiting in cubical shape. The average particle size is found to be between 2-10 µm.

From the XRD result, high peaks of YFe_2 alloy and minor impurity of CaO are observed in this system. The grain size varies from 0.1 µm-0.46 µm. The Magnetic properties of coercivity, retentivity, and magnetization values are 72.256 G (72.256 × 10^{-4} T), 0.73370 emu /g, 23.131 emu/g respectively, as found by vibrating sample magnetometer. It is concluded that this material is a soft magnetic material.

REFERENCES

[1] S.R. Trout, Permanent based on the Lanthanides Raw Materials, Processing and Properties. www.spontaneousmaterials.com.

[2] M. Ilayaraja, L. John Berchmans, Sankara Raman Sankaranarayanan, J. of Metallurgical and Materials Engineering **20** (1), 35-40 (2014).

[3] T.S. Krishanan, Bulletin. Material Science **2** (3), 161-165 (1980).

[4] Guangsi Guo, Guangqiang Li, Liang Liu, J. of Mater. Sci. Technol. **16** (2) 181-182 (2000).

[5] Guangsi Guo, Guangtai Wang, Zhitong Sui, J. Mater. Sci. Technol. **20** (1), 68-70 (2004).

[6] Yingjiao Liang, Yinchang Che, Thermodynamics Data Handbook for Inorganic Substances, Northeastern University Press 514, Shenyang 1993.