Research Article

Characterization and Formation of Rare Earth (Ce) – Transition metal (Ni) alloy by Reduction-Diffusion Process

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Abstract

Cerium Nickel alloy ($CeNi_5$) alloy is the energy storage material, which was produced from its ores directly. The reduction-diffusion process was a new method and less expensive method of formation of rare earth –transition metal alloy compounds from its ore directly. The thermodynamic and kinetics feasible conditions for $CeNi_5$ by reduction – diffusion method in Ce-Ni-Ca system were evaluated. The shrinking unreacted core model (SUCM) theory was used to explain the reduction-diffusion process in which the diffusion is confirmed as rate controlling step. The $CeNi_5$ phase was confirmed by X-Ray Diffraction techniques. The morphology structure of particles and chemical composition of Ce-Ni alloy have been examined by Scanning Electron Microscope technique (SEM) and EDAX technique respectively. The apparent activation energy of $CeNi_5$ was approximately 40 kJ/mol.

Keywords: Shrinking Unreacted Core model theory; Reduction-diffusion process; CeO_2-Ca-Co; Activation energy; Gibbs Free energy.

Introduction

Now days, revolutionized technology have been motivated and introduced for production of rare earth – transition metal alloy; which are growing of interest to the electronics industry and to manufacturers of electro-mechanical devices, with applications in many electronic apparatus, circuits, electric motors, consumer, and defense products. Rare earth Transition intermetallic compounds represent a popular class of rechargeable metal hydrides which rare earth – nickel compounds interest in production of hydrogen storage alloy materials. When considering the less energy – consuming and cheaper process of development of RNi_5 powders for use of rechargeable batteries [1]. The study of magnetic metal investigated that the effect of Ce on the diffusion behavior of Dy-Cu alloys. The addition of Ce reduces the diffusion source melting point and to promote the formation of low-melting alloy phases, benefiting the diffusion behavior. Ce diffusion improves the utilization of Dy, enhances diffusion uniformity, and promotes coercivity improvement. Ce also optimizes and regulates grain boundary phase structure distribution, consistent with magnetic property changes [2].

Rare-earth permanent magnets ($Nd_2Fe_{14}B$) , have been widely used in electric vehicle and wind turbine motors due to their high anisotropy field (Ha), saturation magnetization (Ms) and coercivity (Hc). Cerium (Ce) has gained attention as a potential alternative to neodymium (Nd) due to its high abundance and low cost. In this study, the synthesis of Ce-based $RE_2Fe_{14}B$ (2-14-1) phases was achieved by a modified reduction-diffusion (R-D) process using $REFeO_3$ (RE = Ce, Nd) as a precursor. The precursor was prepared by a solid-state reaction with CeO_2 , Nd_2O_3 , Fe_2O_3 and Fe powders, which is a much more feasible process for mass production and cost-effectiveness. Optimal composition and heat treatment conditions enabled the formation of single-phase Ce-based 2-14-1 particles [3].

Thermodynamics and kinetics analysis of calcium thermal reduction of Nd-Fe-B sludge, the reaction mechanism of the Reduction Diffusion process for sludge waste recovery was clarified. In the RD process, the oxides in the sludge were selectively reduced by Ca at 600–950 °C and the reduced Nd diffused to the surface of the Fe core, forming the Nd-Fe-B alloy, where the formation process included the nucleation stage, the alloy layer high-speed growth stage, and the completion stage. The RD reaction conformed to the unreacted shrinking core model, and its reaction rate control step consisted of a one-way diffusion process for the diffusion of Nd into the Fe core [4]. Understandably that a direct production process is desired by which rare earth oxides and transition metal or metals in some form can be directly converted into an alloy [5]. There are four major possible routes for the production of rare earth–transition 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 in the world. 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 [6].

The reduction-diffusion method has an advantage that is characterized by a direct use of rare earth oxides as raw materials, low cost, and an omission of the halogenation process in metal production. Therefore, reduction – diffusion process is a promising technique with low cost for the preparation of permanent magnet. The RD process is relatively less capital intensive, easy to operate and straightaway yields alloys of the desired composition. [7]. The commonly used preparation process for rare earth- transition metal alloys is the induction melting method, which involves separate extraction and refining the individual metals of high purity, followed by prolonged process at elevated temperatures. In this reasecrh work, we attempted the possibility of preparation of hydrogen storage alloy $CeNi_5$ was prepared directly from a mixture of Cerium Oxide (CeO_2), Nickel powder and Calcium granules by reduction – diffusion process at different temperatures and also investigated the thermodynamic and kinetic feasibility of the formation of alloy.

Experimental

The raw materials (purity 99.55%) of Cerium oxide powder (CeO_2), metallic Nickel powder and calcium granules (in mass) were taken as a stoichiometric ratio. These powders were mixed and made into pellets by hydraulic press at a pressure of 1.44 tons / cm^2. This pellet was kept in a high-density alumina crucible, which was kept in high temperature electrical furnace at 1223 K to 1323 K for 7 hours, under argon (Ar) atmosphere. After the reaction, the product was cooled to room temperature and were taken away from the crucible and then washed with 5% dilute acetic acid and distilled water subsequently, to remove the impurities and CaO . The experimental set up was shown in **Fig. 1**.

Fig. 1. Experimental set up of preparation of Ce-Ni alloy

Characterizations of Ce-Ni alloy system produced at 1273 K

The purified product was then characterized by XRD (PW3040/60 X'pert PRO, PANalytical, Netherlands) to identify the phase composition. The morphology was examined with an instrument of Hitachi, Japan scanning electron microscope S-3000H and also chemical composition of the samples was examined by Energy dispersive-X-ray analyzer.

Results and discussion

Kinetic analysis

Yagi and Kuni in 1995 introduced the Unreacted Shrinking Core Model theory (USCM), reaction of rare earth oxides and transition metal with calcium granules, which acts as a reductant under a category of heterogeneous noncatalytic solid – fluid reactions. The USCM is popular for its ease of application, clear physic-chemical interpretation of the phenomena it describes, and good predictability of many reacting systems [8]. Ajemba and Onukwuli [9] described the USCM as popular for its ease of application, clear physic-chemical interpretation of the phenomena it's describe, and good predictability of many reacting systems. The model assumes that the reaction between fluid and solid takes place on a surface of the reacted core of solid particle and that the fluid reagents must diffuse through the external layer of the gas film and through the porous structure of the reaction product, which forms around the core. Depending on reaction steps –film diffusion, internal diffusion, or surface reaction – may be slower than the others and it controls the reaction rate. To able to use appropriate equations for reaction course, it is practical to know which reaction – controlling step in **Table 1** [9].

Table 1. Time Expressions for Reacting particles according to USCM

Time Expressions	Surface Reaction Controls (a)	Internal Diffusion Controls (b)	Gas Film Diffusion Controls (c)
In terms of Conversions	$kt = \alpha$	$kt = 1-3(1-\alpha)^{2/3} + 2(1-\alpha)$	$kt = 1/(1-\alpha)^{1/3}$

$$CeO_2 + 5\ Ni + 2\ Ca \rightarrow CeNi_5 + 2\ CaO \qquad (1)$$

$$CeO_2 + Ca \rightarrow Ce + 2CaO \qquad (2)$$

$$Ce + Ni \rightarrow CeNi_5 \qquad (3)$$

The processes of eq. (1) consist of two steps: (1) Under reaction temperature Ca vapor quickly diffuses to the surface of CeO_2 granules in porous specimen, where CeO_2 is reduced by Ca and then fresh Ce is produced, which is shown in an eq. 2. (2) The produced Ce diffuses to the adjacent surface of Ni powder, where Ce reacts with Ni to form $CeNi_5$, its nucleus grows at the interface, then the $CeNi_5$ layers are formed gradually is shown in eq. 3. The mode of Ce vapor diffusing is by the gas phase. There are two ways for Ce to transfer on the surface of Ni powder.

If the reaction is controlled by resultant product layer internal diffusion, this formula is derived from the relation between the rate and time, which is satisfied by Unreacted Core Model Theory.

$$kt = 1-3(1-\alpha)^{2/3} + 2(1-\alpha) \qquad (4)$$

Where, k = rate constant, sec^{-1}, t= time (sec), α = Conversion rate

The Conversion rate or rate of reduction- diffusion can be calculated by [10]

$$\text{Rate of Reduction-Diffusion } (\alpha) = M_Y / M°_Y \times 100\% \qquad (5)$$

Where M_Y is the weight of Ce in $CeNi_5$ formed by the diffusion of Ce into Ni and $M°_Y$ is the weight of Ce in the raw materials.

Using the conversion rate in eq. (5), the reaction rate constant can be calculated for 7 hrs for conversion of reactant to the product at different temperatures such as 1223 K is 0.346, 1273 K is

0.3002 and 1323 K is 0.2539 respectively. Using the conversion rate, to find the rate constant by eq. (4), it gives 2.954×10^{-5} sec^{-1} at 1223 K, 3.454×10^{-5} at 1273 K and 3.6646×10^{-5} at 1323 K respectively. From the **Fig. 2,** described that rate constant of these reactions, it increases the rate constant with increasing the temperatures, it favors forward reaction and kinetic feasibility to produce the product.
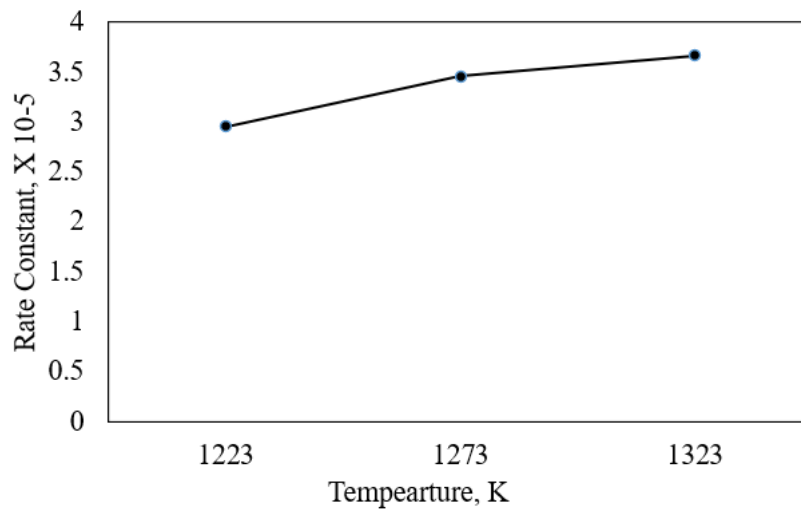
Fig. 2. Rate Constant for Ce-Ni alloy by Unreacted Shrinking core model theory

Apparent activation energy

The activation energy of a chemical reaction can also be determined algebraically using Arrhenius equation. For each rate constant, Arrhenius equation can be written as eq. (6).

$$E_a = T_1 T_2 / (T_1 - T_2) . R \ln (k_1/k_2) \qquad (6)$$

Using these values and substitute in eq. (6), we get activation energy is approximately 40.48 KJ/mole.

Gibbs free energy relation

The Ce-Ni binary system was studied, even though, there is no data of formation of free energy of Ce-Ni could be used.

In the R-D process preparation, the following reaction was considered,

$$CeO_2 + 5 Ni + 2 Ca \rightarrow CeNi_5 + 2 CaO \qquad (7)$$

According to the Hess law of heat summation eq. (7) can be split into:-

$$Ce + 5 Ni \rightarrow CeNi_5 \qquad (8)$$

$$CeO_2 + Ca \rightarrow Ce + 2CaO \qquad (9)$$

$$Ca_{(l)} = Ca_{(g)} \qquad (10)$$
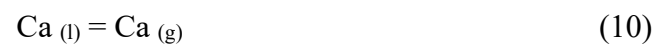
Assuming the CeNi$_5$ as an ideal solution, the entropy change of CeNi$_5$ formation at 298 K could be written as

$$\Delta S^o_{298} = -R (X_A \ln X_A + X_B \ln X_B) \qquad (11)$$

From the eq. (8),

$$\Delta S^o_{298} = -R (1/6 \ln 1/6 + 5/6 \ln 5/6) \qquad (12)$$

$$\Delta S^o_{298} = 3.723 \text{ J / deg / mole} \qquad (13)$$

Assume the thermal heat capacity of Ce-Ni obeys the Newmann-Kopp's rule, ΔCp of eq. (8) is zero, and the enthalpy change of eq. (8) at 298 K becomes 46905.249 J / mole.

The formation free energy of CeNi$_5$ could be obtained from eq. (8)

$$\Delta G^o{}_{298\,(2)} = 46905.249 - 3.722T \qquad (14)$$

Using given data, equation (9),

$$\Delta S^o{}_{298\,(3)} = \{S^oCe + 2\,^oS\,CaO\} - \{S^oCeO_2\} \qquad (15)$$

$$\Delta S^o{}_{298\,(3)} = -2.4 \text{ J / mol/ K} \qquad (16)$$

The enthalpy change of formation at 298 K in eq. (9),

$$\Delta H^o{}_{298} = (\Delta H^o{}_{products} - \Delta H^o{}_{reactanst} \qquad (17)$$

$$\Delta H^o{}_{298(3)} = -209300 \text{ J / mole} \qquad (18)$$

The Gibbs energy formation of eq. (9) at 298 K is,

$$\Delta G^o{}_{298(3)} = -209300 - 2.4 \text{ T} \qquad (19)$$

From the equation (10), the Gibbs energy formations at 298 K can be written as (19),

$$\Delta G^o{}_{298(4)} = 117800 - 154.9 \text{ T} \qquad (20)$$

Rearranging the equation (14), (19) and (20), get the Gibbs energy formation of a reaction at 298 K is

$$\Delta G^o{}_{298(1)} = -280194.751 - 161.023 \text{ T} \qquad (21)$$

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

$$\Delta G = \Delta G^o{}_{298(1)} + RT \ln (p_{ca} / P^o)^{-3} \qquad (22)$$

Where the p_{ca} is the vapour pressure of calcium and P^o is the standard atmospheric pressure (101325 Pa), $\log P_{ca} = -8.92 \times 10^3 \, T^{-1} - 139\log T + 11.58$ kPa. [11]. $\qquad$ (23)

Using the eq. (22), the values of Gibbs free energy of formation of reactions (ΔG) at 1223 K, 1273 K and 1323 K are obtained: -409.752 KJ / mole, -417.844 KJ / mole, -420.390 KJ / mole respectively.

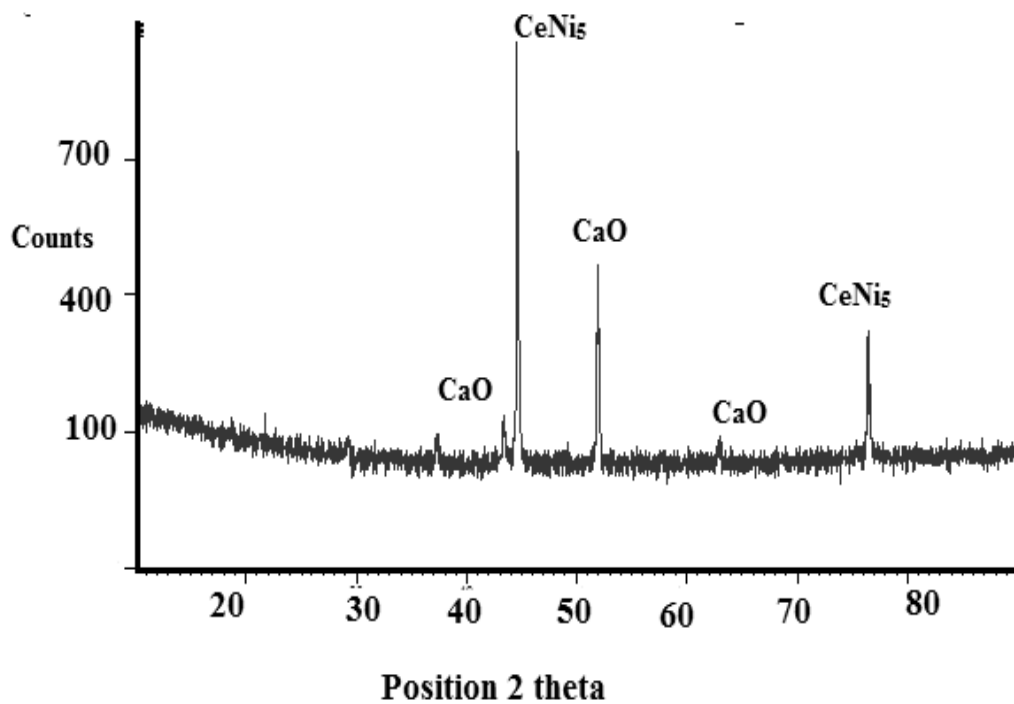### XRD results of Ce-Ni alloy system produced at 1273 K

The XRD patterns for the specimens at 1273 K for 7 hours. **Fig. 3.** shows that high intensity peaks of Ce-Ni and CaO and minor impurities are also observed in this system.

$$T = k * \lambda / B * Cos\,\theta_B \qquad (24)$$

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. Comparing the result of Ce-Ni alloy JCPDS file shows the peaks, however, the $CeNi_5$ phase is examined in the XRD pattern. The full-width at half-maximum (FWHM) of the $CeNi_5$ peak was used in the Scherrer eq. (24) to independently estimate the average grain size of ranging from 0.1μm to 0.8 μm.

SEM analysis of Ce-Ni alloy system produced at 1273 K

SEM micrograph reveals that the particle size and morphology of the crystal in the **Fig. 4**, The $CeNi_5$ grains examined in the pellets after the reduction-diffusion process. The rare earth – intermetallic products ($CeNi_5$) have been examined and observed to be in shape of hexagonal. In the morphology study, $CeNi_5$ was examined in dark region and also CaO was examined in brighter region. The $CeNi_5$ particle size analysis has been evaluated at 20 μm standard size. The grain size of Ce-Ni has been observed in non-uniform structures and shapes.
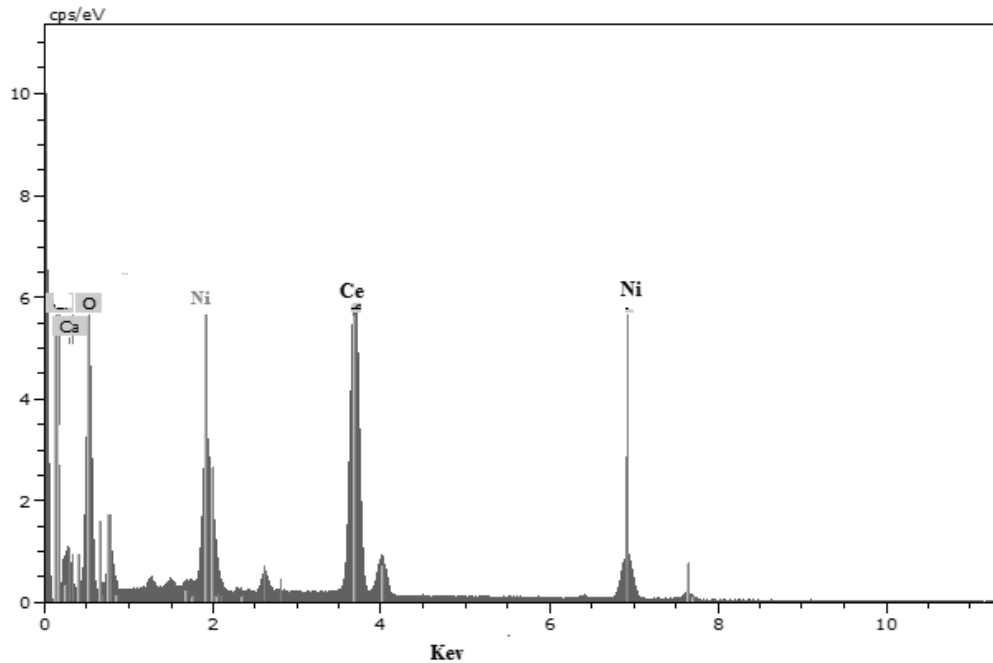
Fig. 3. XRD Pattern of Ce-Ni alloy system produced at 1273 K
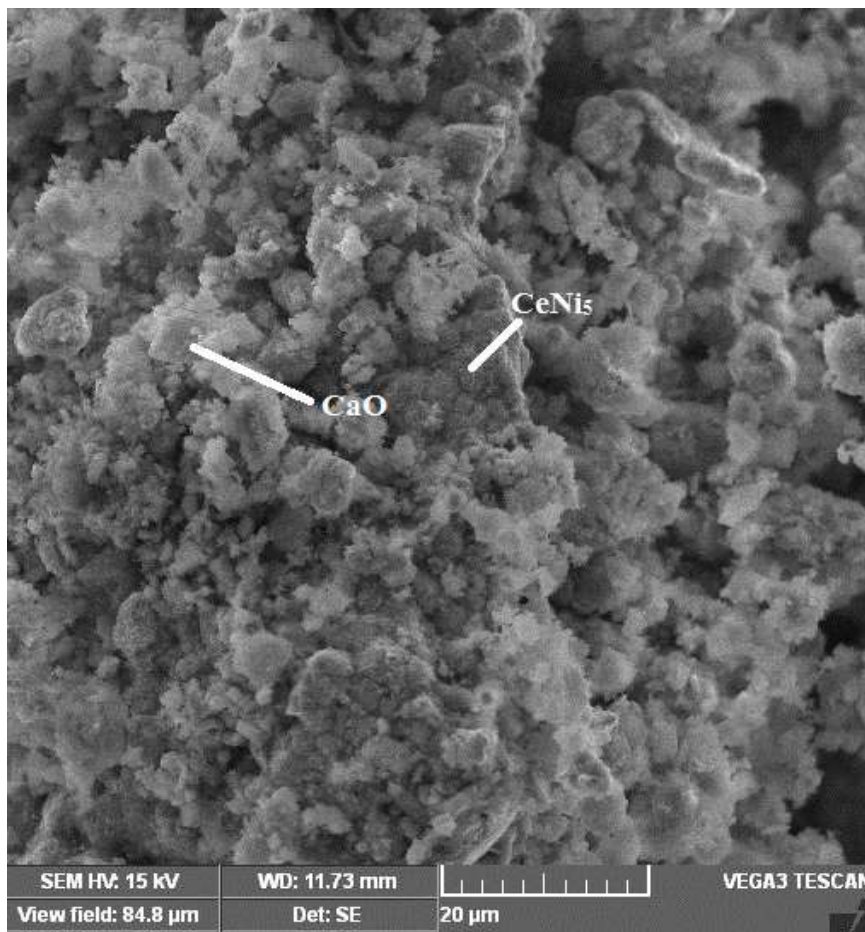
Fig. 4. Morphology of Ce-Ni alloy system produced at 1273 K

EDAX analysis of Ce-Ni alloy system produced at 1273 K

Fig. 5 shows the EDAX spectrum of the synthesized $CeNi_5$ rare earth - intermetallic compound. This technique is used to examine the chemical composition of individual elements present in Ce-Ni alloy. The X-ray energy is the characteristic of generating atom and therefore, detection of X-rays emitted provides the signature of the atoms present in the compound. The result analyzed with EDAX shows that the atomic percentage of $CeNi_5$, Ce= 15 %, Ni = 75 %, and remaining impurities 10 % of CaO are present respectively.

Fig. 5. EDAX spectrum *of Ce-Ni alloy system produced at 1273 K*

Conclusions

From this research, it is concluded that study the thermodynamic and reaction kinetics feasibility to produce the energy storage materials of $CeNi_5$ alloy by reduction diffusion process. The values of Gibbs free energy have been obtained at different temperatures were at 1223 K, 1273 K and 1323 K were -409.752 KJ / mole, -417.844 KJ / mole, -420.390 KJ / mole respectively. The rate constant and conversion rate can be evaluated by an unreacted shrinking core model theory. From kinetics, the rate constant is increased with increasing the temperature and the reaction has favored the conversion of product. The values of rate constant at different temperatures are 2.954×10^{-5} sec^{-1} at 1223 K, 3.454×10^{-5} at 1273 K and 3.6646×10^{-5} at 1323 K respectively. The apparent activate energy is required to decompose the reaction was found by Arrhenius equation is approximately 40 KJ / mole. The average grain size of $CeNi_5$ was examined by X-ray diffraction technique and ranges from 0.1 to 0.8 μm by scherrer equation. The grain size is in hexagonal and the arrangement of particles in non-uniform and shapes has been found by SEM analysis. This method is a novel technique for preparation of alloy by reduction – diffusion process directly from its ores when compare with conventional methods in the future.

Conflict of interest

The authors declare no conflict of interest.

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