Journal of Alloys and Compounds 705 (2017) 462–467

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

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

Investigation of amorphous phase formation in Fe-Co-Si-B-P - Thermodynamic analysis and comparison between mechanical alloying and rapid solidification experiments

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ARTICLE INFO

Article history:
Received 5 January 2017
Received in revised form
7 February 2017
Accepted 10 February 2017
Available online 14 February 2017

Keywords:
Glass forming ability
Mechanical alloying
Iron-base amorphous alloys
Extended Miedema model

ABSTRACT

In recent years, amorphous alloys have received a considerable attraction because of their physical, mechanical and magnetic properties. Fe-Co alloy system has good soft magnetic properties (high magnetic saturation and high Curie point) which makes it suitable for high temperature magnetic applications. In this paper, the effect of different elements on glass forming ability (GFA) of Fe-Co system was evaluated based on Meidema semi-empirical model and the results were compared to mechanical alloying (MA) experiments. Si, B and P seem to be good elements to be added to Fe-Co alloys with respect to thermodynamics and kinetics requirements. Calculations based on extended Miedema model showed that enthalpy and Gibbs free energy changes for solid state amorphisation of $Fe_{70}Co_7Si_8B_8P_7$ were −179 (kJ mol^{-1}) and −181 (kJ mol^{-1}) respectively, but MA experiments in three different routes did not lead to amorphisation in this system. Also comparison between MA and melt spinning (MS) techniques showed GFA in both techniques are completely different.

1. Introduction

Metallic amorphous alloys are advanced materials that have interesting combination of physical, chemical, mechanical, and magnetic properties which cannot be obtained in conventional crystalline alloys [1]. These unique characteristics make them attractive for a variety of applications. The ability of producing nano-crystalline alloys with high controllability from crystallization of amorphous phase, is another importance of amorphous materials. Consequently there has been a lot of interest in understanding the structure, forming ability and properties of these materials [2]. In general, there are several methods for fabrication of amorphous alloys among which rapid solidification process (RSP) and mechanical alloying (MA) are more important than others. In recent years, progression and development trends in the field of amorphous alloys have been toward to alloy systems such as Iron-based amorphous alloy with high performance while having low cost [1]. Among the many Iron-based amorphous alloys, Fe—Co alloys have a special importance due to their interesting soft magnetic properties such as high magnetization saturation [3] and also high Curie temperature [4] that making them suitable for the high temperature applications such as new generation turbine engines and recording media [5–7]. For these applications good mechanical properties are also important. A combination of good mechanical properties beside good soft magnetic properties is a challenge for soft magnetic materials which can be achieved in amorphous state. Fe-Co alloys in amorphous state keep their good soft magnetic properties with a high value of in yield strength (~4000 MPa) [1,8]. Amorphous Fe-Co based alloys were synthesized by RSP process successfully [1,9] but MA amorphisation of Fe-Co alloys seems to be difficult due to the small negative heat of mixing (−2 kJ/mol) and low mutual solubility at room temperature [10,11]. However MA amorphisation in Fe-Co alloys can be improved by adding suitable elements [12,13]. Based on experimental evidence, two criteria for the solid-state amorphisation reaction are developed; A large negative heat of mixing, ΔH_{mix}, between alloying elements as well as a large difference between diffusion coefficient of one element in the others [14]. The latter is attained where there is a large difference in atomic size elements. In the present paper, the effect of addition of different metalloid elements on amorphisation of Fe-Co system was investigated. The amorphisation ability was predicted based on thermodynamic analysis (thermodynamic criteria) by Miedema's semi-empirical model [15] and atomic size mismatch (kinetic criteria). The

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http://dx.doi.org/10.1016/j.jallcom.2017.02.100
0925-8388/

amorphous phase formation enthalpy and Gibbs free energy change were calculated based on Extended Miedema's model [16]. The results were compared with those obtained by mechanical alloying process. Finally there is also comparison between MA and MS techniques experiments in Fe-Co-Si-B-P alloy system.

2. Materials and methods

Mixture of Iron (Fe), Cobalt (Co), Silicone (Si), Boron (B) and phosphorous (P) powders with $Fe_{70}Co_7Si_8B_8P_7$ composition were MAed in a high energy planetary ball mill (Fritsch P7) at room temperature. Table 1 shows the characteristics of raw materials. The vial was hardened chromium steel with 120 ml volume and balls were hardened high carbon steel with three different size of 10 (#5), 15 (#6) and 18 mm (#2). Ball to powder weight ratio and rotation speed were 10:1 and 320 rpm respectively. In order to avoid oxidation, MA process was carried out under Ar atmosphere. Phase analysis was performed using X-ray diffractometer (Philips XPERT-MPD) with Cu Kα radiation (λ = 0.1542 nm), time per step of 0.05 s at 2Θ = 10-100°. MA was performed in three different routes as demonstrated in Table 2. Miedema's Extended model was used to calculate the enthalpy and Gibbs free energy change of amorphisation in $Fe_{70}Co_7Si_8B_8P_7$ alloy system.

3. Results and discussion

3.1. Selection of suitable elements based on mixing enthalpy (ΔH_{mix}) and atomic size mismatch

ΔH_{mix} was calculated using Miedema's semi-empirical model [15] to find which element can produce a negative ΔH_{mix}, required for MA amorphisation with Fe in solid state. The Gibbs free energy change (ΔG) can be expressed as:

$$\Delta G = \Delta H - T\Delta S \quad (1)$$

where ΔH is mixing enthalpy change, T, ambient temperature and ΔS is mixing entropy change. For a binary ideal solid solutions ΔS can be written as:

$$\Delta S = -R(X_A \ln X_A + X_B \ln X_B) \quad (2)$$

$$X_A + X_B = 1$$

where R is universal gas constant and X_A and X_B are atomic concentrations in solid solution.

According to Miedema's semi-empirical model the heat of mixing in A-B system is due to the, electronegativity difference (a negative term) and electron density difference (a positive term) between two components. In Miedema's semi-empirical model, ΔH_{AB}, includes three parts:

$$\Delta H_{total} = \Delta H_{Chemical} + \Delta H_{Elastic} + \Delta H_{Structural} \quad (3)$$

where $\Delta H_{Chemical}$ is chemical enthalpy, $\Delta H_{Elastic}$, elastic enthalpy and $\Delta H_{Structural}$, structural enthalpy.

Table 1
Characteristics of raw materials.

Raw materials	Purity (%)	Particle size (μm)	Structure
Fe	99.00	<100	Crystalline
Co	99.8	<50	Crystalline
Si	99.9	<50	Crystalline
B	99.9	<30	Crystalline
P	98	<30	Amorphous

Table 2
MA routes.

Routes	Explains
Route A	Continuous MA for 160 h
Route B	MA with stearic acid as a process control agent (PCA) for 100 h
Route C	MA for 50 h + annealing at 800 °C for 1 h + further MA for 60 h

The chemical contribution is due to difference in bonding energy of atoms of components in the initial and mixing states. $\Delta H_{Elastic}$ and $\Delta H_{Structural}$ contributions are due to atomic size difference and the difference in valence electrons and crystal structure of solvent and solute atoms, respectively. The chemical contribution of ΔH_{total} is calculated as follow:

$$\Delta H_{AB}^{(Chemical)} = X_A X_B \left[f_A^B \, \Delta H_{B\ in\ A}^{(Sol.)} + f_B^A \, \Delta H_{A\ in\ B}^{(Sol.)} \right] \quad (4)$$

f_A^B, f_B^A and $\Delta H_{B\ in\ A}^{(Sol.)}$ are the concentration function and solution enthalpy for mixing B in A respectively that defined as:

$$f_A^B = X_A^S \left[1 + \gamma \left(X_A^S X_B^S \right)^2 \right] \quad (5)$$

$$f_B^A = X_B^S \left[1 + \gamma \left(X_A^S X_B^S \right)^2 \right] \quad (6)$$

$$\Delta H_{B\ in\ A}^{(Sol.)} = \left[\frac{V_A^{\frac{2}{3}}}{\left(n_{ws}^{-\frac{1}{3}} \right)_{av}} \right] \left\{ -p(\Delta\phi^*)^2 + Q \left(\Delta n_{ws}^{\frac{1}{3}} \right) - R^* \right. \quad (7)$$

Also X_A^S and X_B^S defined as:

$$X_A^S = \frac{X_A V_A^{\frac{2}{3}}}{X_A V_A^{\frac{2}{3}} + X_B V_B^{\frac{2}{3}}} \quad (8)$$

$$X_B^S = \frac{X_B V_B^{\frac{2}{3}}}{X_A V_A^{\frac{2}{3}} + X_B V_B^{\frac{2}{3}}} \quad (9)$$

where V is the molar volumes of atoms, ϕ^* is the work function of B, n_{ws} is the electron density, P, Q and R^* are empirical constants and γ is 0 for solid solution, 5 for amorphous phase and 8 for intermetallic compound. R^* can be calculated from existing data [17–19]. P equal 14.2 and 10.7 transition and non-transition metals respectively. It should be noted that P/Q = 9.4 and R^* is taken in account only for those systems which include one transition metals and non-transition metals. The required parameters for calculations of thermodynamics values are shown in Table 3. Phosphorus parameters are extended from Ref. [18]. Solution enthalpy of some elements in Iron and atomic size mismatch are shown in Tables 4 and 5 respectively.

According to Tables 4 and 5, the negative heat of mixing of Co with Fe (−2 kJ/mol) and the small mismatch between their atomic radii and electronegativity make the formation of Fe-Co alloys easy and feasible in MA. Many researches showed that formation of Fe-Co alloys in wide any range of Co (10–90 wt%) easily and in a short time in MA [20]. According to values given in Tables 4 and 5, Zr, Ti, Al, Nb, Si, B, P and C have required thermodynamics and kinetic values to be add to Fe-Co alloys for successful amorphisation. In contrast elements such as Cu, La and Hf because of their positive heat of mixing with Fe attend to