Journal of Non-Crystalline Solids xxx (xxxx) xxx–xxx

Contents lists available at ScienceDirect

Journal of Non-Crystalline Solids

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

Glassy blast furnace pig iron and design of other glassy compositions using thermodynamic calculations

N. Mahata[a], A. Banerjee[b], P.K. Rai[a], P. Bijalwan[b], A.S. Pathak[b], S. Kundu[b], M. Dutta[b], K. Mondal[a,*]

[a] Department of Materials Science and Engineering, Indian Institute of Technology Kanpur, UP, India - 208016
[b] Research & Development and Scientific Services, Tata Steel Limited, Jamshedpur, Jharkhand, India – 831001

ARTICLE INFO

Keywords:
Metallic glass
Glass forming ability
Pig iron
Melt-spinning

ABSTRACT

Formation of metallic glass largely depends on the composition of the alloy system and inherent glass forming ability (GFA). Among all the relevant GFA criteria, GFA parameter, P_{HSS}, gives better quantitative description to explain higher GFA in multicomponent systems. Present work shows a set of glass forming alloys designed with the help of some GFA parameters including P_{HSS} using a raw blast furnace (BF) grade metal, popularly known as pig iron, in the range of 75–100 wt% of the total alloy weight and addition combination of alloying elements (B, P, Nb, Cr, Mo). Good glass forming ability of the blast furnace hot metal (direct from blast furnace containing impurities) as determined by thermodynamic calculation has been experimentally validated by making its glassy ribbons by melt spinning in air as well 1 mm diameter partially glassy rod as confirmed by X-ray diffraction (XRD), transmission electron microscopy (TEM) and differential scanning calorimetry (DSC) studies.

1. Introduction

Fe-based glassy alloys have gained huge attention for their exciting combination of properties, like high strength, high stiffness, excellent corrosion resistance and great soft magnetic properties [1–3]. On the contrary, metallic glasses as a whole show very little tensile ductility even though it has extremely high (~few GPa) yield strength. However, considerable compressive plasticity has been reported in many metallic glasses [4–5]. Therefore, structural application of glassy alloys has been thought to be realized if it is used as corrosion and wear resistant coatings [6–8].

However, even after significant progresses on amorphous alloys in terms of finding newer glassy alloys with excellent glass forming ability as well as combination properties [9–13], the practical applications of metallic glasses are still very limited due to high cost of production and most of bulk amorphous alloys are fabricated in laboratory scale using high purity raw materials in clean atmosphere. Impurities in raw materials or oxidation during processing can significantly decrease the GFA of alloy systems [14]. In general, the GFA parameters, such as T_{rg} [15], ΔT_x [16], γ [17], α and β [18] of any composition can be found out after synthesizing the alloy by trial and hit method and require experimental validation to prove the glass forming nature of the selected composition. Hence, such GFA parameters are not predictive in nature.

In order to understand the glass formation in a particular alloy system, it is important to understand the GFA of the particular composition with reasonable accuracy. Recently, Chattopadhyaya et al. [19] have put up a nice review article, where it has been clearly shown that there could be semi-predictive as well predictive approaches in order to judge GFA of a particular composition. Inoue et al. [20] have proposed three empirical rules for GFA in metallic glasses: (i) The atomic size difference between major constituents must be > 12%, (ii) there must be a negative mixing enthalpy between constituents, and (iii) the alloy composition must include more than three elements. Mismatch entropy normalized by Boltzmann constant (S_σ^{alloy}/k_B) and chemical mixing enthalpy (ΔH^{chem}) correspond to the rule (i) and (ii) of the empirical rules. Critical values of ΔH^{chem} and S_σ^{alloy}/k_B require to be –15 KJ/mol and 0.1, respectively, to obtain high GFA for typical multicomponent systems [21]. But these parameters are limited to ternary alloy systems only and found to be insufficient to predict GFA in multicomponent systems containing more than three elements. However, P_{HSS} parameter gives better quantitative analysis of GFA in multicomponent systems [22]. Moreover, higher negative value of P_{HSS} indicates better GFA. It is always better to use predictive approach to bring down the number of actual experimental trials, which later can be used for the judgment of semi-predictive glass forming ability. Predictive approaches are mainly decided by the thermodynamics and kinetic understanding of the phase transformations in glassy system as well as structure of the alloy.

Cost factor and highly pure metal combination as well as controlled

* Corresponding author.
E-mail address: kallol@iitk.ac.in (K. Mondal).

https://doi.org/10.1016/j.jnoncrysol.2018.01.029
Received 16 November 2017; Received in revised form 11 January 2018; Accepted 15 January 2018

Table 1
Typical composition of pig iron (BF metal).

Considered composition (weight %)	Considered composition (atom %)
C-3.5	C-14.04
P-1.4	P-2.18
Si-2.0	Si-3.43
Mn-0.5	Mn-0.44
S-0.030 (neglected)	S-0.00
Fe- 92.6	Fe-79.91

atmosphere associated with making of metallic glass are major impetus to the use of glassy alloys in practical applications. Hence, choice of using relatively impure but cheaper metals and alloys like pig iron as base raw material with ease of processing under ambient atmosphere for making glassy alloys with good GFA would be of great technological advantage. The present work explores the potential of formation of glassy alloys using the pig iron, a regular BF product with presence of impurities in the form of undesired elements like S, entrapped slag and oxide particles etc. as base raw material, and subsequent modification in composition of the pig iron by doing a series of alloy design via predictive approach as mentioned earlier and further elaborated in subsequent discussion. The pig iron in the present work contains ~2.18 at.% P and 3.43 at.% Si, which are considered to be high compared to steel or cast iron. Moreover, presence of high P and Si help in increasing the GFA [23–24]. The typical composition of pig iron is mentioned in Table 1. Therefore, pig iron has been chosen as base metal for designing different glassy compositions by using predictive models. In addition, the authors also put forward the justification for these newly designed alloys on the basis of the predictive model. Later, experimental validation was carried out to justify the use of pig iron for synthesizing new Fe based glassy alloys with comparable GFA than the alloys already reported in literature.

2. Theory

2.1. Predictive approach: calculation of the thermodynamic and topological parameters

2.1.1. Mixing enthalpy

ΔH^{chem} is calculated using extended regular solution model

$$\Delta H^{chem} = \sum_{\substack{i=1,\\ j\neq i}}^{n} \Omega_{ij} c_i c_j$$

Here, Ω_{ij} is regular solution interaction parameter between i-th and j-th component and it is taken as a constant, c_i is the composition of i-th element. Ω_{ij} is substituted with the following relation: $\Omega_{ij} = 4 \times \Delta H_{AB}{}^{mix}$, where $\Delta H_{AB}{}^{mix}$ is mixing enthalpy of A and B resulting from Miedema's macroscopic model for binary alloys and the coefficient four is due to equiatomic composition in binary A-B system [25].

2.1.2. Mismatch entropy

The mismatch entropy arises due to the atomic size difference of the constituting elements in the alloy system is calculated using Mansoori empirical model [26].

$$S_\sigma = k_B\left[\frac{3}{2}(\zeta^2-1)y_1 + \frac{3}{2}(\zeta-1)^2 y_2 - \left\{\frac{1}{2}(\zeta-1)(\zeta-3)+\ln\zeta\right\}(1-y_3)\right]$$

where, k_B is Boltsmann constant, $\zeta = 1/(1-\xi)$ where ξ is packing fraction. In present study ξ is fixed to be 0.64, which implies a dense random packing. Dimensionless parameters y_1, y_2, y_3 and have a relation $y_1 + y_2 + y_3 = 1$

$$y_1 = \frac{1}{\sigma^3}\sum_{j>i=1}^{n}(d_i + d_j)(d_i - d_j)^2 c_i c_j$$

$$y_2 = \frac{\sigma^2}{(\sigma^3)^2}\sum_{j>i=1}^{n}(d_i d_j)(d_i - d_j)^2 c_i c_j$$

$$y_3 = \frac{(\sigma^2)^3}{(\sigma^3)^2}$$

$$\sigma^k = \sum_{i=1}^{n} c_i d_i^k \qquad k = 2,\ 3$$

d_i is the atomic diameter of i-th element and quoted from data book [27].

2.1.3. Configurational entropy

Configurational entropy is calculated based on Stirling's approximation [28]

$$\Delta S_{config} = -R\sum_{i}^{n} c_i \ln c_i$$

where R is the universal gas constant and c_i is the atomic fraction of i-th element.

2.1.4. P_{HSS}

P_{HSS} parameter developed by Rao et al. [22] for predicting GFA

$$P_{HSS} = \Delta H^{chem}(S_\sigma/k_B)(S_{config}/R)$$

The above mentioned GFA parameters are calculated for some good Fe-based glass forming alloys reported in literature [29–31] and same GFA parameters for the new designed pig iron based alloys calculated by using the predictive approach have been compared. It also validates the thermodynamic calculations in order to improve the glass forming ability of the high phosphorous BF metal with a minor adjustment of the composition by adding one or combination of alloying elements, like P, B, Nb, Mo, Cr etc. It is important to mention that the use of BF metal has been varied from 75 to 100 wt% with additional alloying to achieve excellent GFA. Here, the alloying additions have been selected based on their effects on GFA and corrosion resistance in Fe based amorphous systems. It is reported in literature that Cr is the most potential element to increase the corrosion resistance of iron based amorphous alloy systems [32]. Nb and Mo addition to amorphous alloys promotes both GFA and corrosion resistance [33–34]. The high GFA is attributed due to generation of new atomic pairs with large negative heat of mixing values [35]. Metalloids, such as P, B are generally added to Fe based amorphous alloys to enhance the GFA, but they also improve the corrosion resistance of Fe-Cr amorphous alloy systems [36].

The comparative GFA parameters of the Fe-based amorphous alloys reported in literature and BF metal (pig iron) are shown in Table 2. It shows that the critical thickness (as taken from literature) increases with decreasing value of P_{HSS}. Moreover, other GFA parameters are also indicative of considerably better glass forming ability. Even the pig iron itself has more negative P_{HSS} value than some of the good Fe-based glassy alloys.

Tables 3–7 show the new compositions, which have shown higher GFA than some of the very good Fe-based glass systems already reported in literature [29–31]. Table 3 shows the GFA parameters calculated for the alloys with increasing P content (P - 2.5 wt% to 11.4 wt %) in the as received BF metal. It clearly shows P_{HSS} value decreases with increasing phosphorus content in the alloy. A prediction can be made from this correlation that the critical thickness as well as GFA would also increase along with increase in P content. From the binary phase diagram of Fe-P (Fig. 1 [37]), it is clear that the high P takes the alloy closer to the deep eutectic, which is beneficial to enhance the GFA [38]. Other GFA parameters for these alloys as mentioned in Table 2