Formation and soft magnetic properties of Co (-Fe)-Si-B-Nb bulk metallic glasses in relation to clusters

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Abstract. Bulk metallic glass formations in Co-based alloy systems are investigated with the guidance of our cluster line approach and minor-alloying principle. Basic ternary alloy compositions in Co-B-Si system are first determined by cluster lines defined by linking special binary clusters to third elements. Then these basic ternary alloys are further minor-alloyed with 4-5 at. % Nb and bulk metallic glasses of 3 mm in diameter are formed in (Co8B3-Si)-Nb, Co8B3 being dense-packed cluster. The bulk metallic glasses are expressed approximately with a unified simple composition formula: (Co8B3)(Si,Nb). Finally a quantity of Fe substitution for Co further improves the glass-forming abilities and these Co-Fe-based quinary bulk metallic glasses have good soft magnetic properties with high saturation magnetization $I_s$, up to 0.98T, and low coercive force $H_c$, below 6 A/m.

1. Introduction
Co-based bulk metallic glasses (BMGs) are drawing increasing attention due to their superior mechanical and soft magnetic properties [1, 2]. However, as compared with Pd-, Zr- and Cu-based BMGs, the Co-based ones have relatively weak glass forming abilities (GFAs) and are formed only in multi-component systems [3]. Furthermore, these BMGs are composition-sensitive and the BMG-forming ranges are quite small. Therefore, the composition design is of great importance for developing new Co-based BMGs with large GFAs. The existing empirical rules [3-5], however, fail in providing quantitative composition guidelines in such complex systems.

In this paper, we will introduce the cluster line approach into the Co-B-Si based BMG-forming systems. Such an approach has successfully guided the composition design of Zr-, Cu-, Sm- and Y-based BMGs [6-9]. In addition, minor-alloying by elements with atomic sizes different from the main constituent elements can dramatically improve the GFAs of metallic glasses [6, 10]. Therefore, the basic ternary Co-B-Si compositions are first designed by using cluster lines. Then, the basic Co-B-Si compositions are minor-alloyed with a fourth element Nb and finally, the base element Co is partially substituted by Fe. Furthermore, the soft magnetic properties of Co-based BMGs are also studied.

2. Composition design using cluster line and minor-alloying
A cluster line in a ternary phase diagram is a straight composition line linking a binary cluster composition to the third element. The specific binary cluster is a nearest-neighbor coordination polyhedron that usually exists as a local structure of crystalline phases.

The origin of such cluster lines is traced to the negative enthalpies of mixing of the constituent elements in ternary BMG-forming systems. In Co-B-Si ternary system, the enthalpies of mixing of Co-B, Co-Si and B-Si are respectively $\Delta H_{\text{Co-B}} = -24 \text{ kJ/mol}$, $\Delta H_{\text{Co-Si}} = -38 \text{ kJ/mol}$ and $\Delta H_{\text{B-Si}} = -14 \text{ kJ/mol}$ [11]. The enthalpies of mixing of the Co-B and Co-Si pairs are significantly larger than that of B-Si pair, which favors to form the separated Co-B and Co-Si binary clusters in ternary structures. Due to the similarity of local structures in metallic glasses and competing crystalline phases [12], the local structures of Co-B, Co-Si and Co-B-Si crystalline phases are analyzed and from which a series of binary clusters are derived. The Co-rich Co-B clusters centered by B are respectively CN10 capped Archimedean antiprism $\text{Co}_8\text{B}_3$, CN9 side-capped trigonal prisms $\text{Co}_7\text{B}_3$ and $\text{Co}_9\text{B}_3$, CN11 capped trigonal prism $\text{Co}_9\text{B}_3$. And the Co-rich Co-Si cluster is a CN12 cube-octahedron $\text{Co}_{12}\text{Si}$ centered by Si.

Cluster lines $\text{Co}_7\text{B}_3$-$\text{Si}$, $\text{Co}_8\text{B}_3$-$\text{Si}$, $\text{Co}_9\text{B}_3$-$\text{Si}$, $\text{Co}_{9}\text{B}$-$\text{Si}$ and $\text{Co}_{12}\text{Si}$-$\text{B}$ are then constructed in the basic ternary Co-B-Si system, as shown in figure 1. The Co-B cluster lines and the $\text{Co}_{12}\text{Si}$-$\text{B}$ cluster line intersect at four basic ternary compositions $\text{Co}_{66.2}\text{B}_{28.3}\text{Si}_{5.5}$, $\text{Co}_{68.6}\text{B}_{25.7}\text{Si}_{5.7}$, $\text{Co}_{70.6}\text{B}_{23.5}\text{Si}_{5.9}$ and $\text{Co}_{83.7}\text{B}_{9.3}\text{Si}_{7}$. These compositions can be expressed in a more explicit manner using a cluster-glue atom formula, $\text{Co}_{66.2}\text{B}_{28.3}\text{Si}_{5.5}$, $\text{Co}_{68.6}\text{B}_{25.7}\text{Si}_{5.7}$, $\text{Co}_{70.6}\text{B}_{23.5}\text{Si}_{5.9}$ and $\text{Co}_{83.7}\text{B}_{9.3}\text{Si}_{7}$.

![Figure 1. Schematic composition chart of Co-B-Si ternary system. Cluster lines and intersection points are shown.](image)

### 3. Experimental

Ingots of Co-Si-B, Co-Si-B-Nb and Co-Fe-Si-B-Nb alloys were prepared by using arc melting the mixtures of constituent elements under argon atmosphere. The purities of elements are 99.99 wt% for Co and Fe, 99.5 wt% for B, 99.9 wt% for Si and 99.96 wt% for Nb respectively. Alloy rods with a diameters of 2 mm and 3mm with a total length of 40 mm were prepared by means of copper mould suction casting. Structural identification of these alloys was carried out by means of X-ray diffractometry (XRD) on the bottom of the rods using the Cu $K_\alpha$ radiation ($\lambda = 0.15406$ nm). Differential scanning calorimetry (DSC) and differential thermal analysis (DTA) are employed to study the thermodynamic behaviors of the BMGs at a heating rate of 0.33 K/s. Magnetic properties of saturation magnetization ($I_s$) and coercive force ($H_c$) were measured with a vibrating scanning magnetometer (VSM) under an applied field of 800 kA/m, a B-H loop tracer under a field of 800 A/m.

### 4. Results and discussions

A good metallic glass usually possesses dense-packed local atomic cluster structures. Miracle et al [13] proposed a topologically efficient cluster-packing structural model and calculated the critical
radius ratios $R^*$ values for ideal dense-packed clusters, where $R^* = r_0/r_1$, $r_0$ being the radius of the central atom and $r_1$ the radius of the $1^{st}$-shell atoms. We calculated the radius ratio $R$ of Co-B and Co-Si clusters taking the Goldschmidt radii of Co, B, and Si as 0.125 nm, 0.098 nm and 0.132 nm respectively. There exists difference between actual and ideal clusters with the same coordination number (CN), represented by $\Delta = (R-R^*)/R^*$. Take the cluster Co$_{8}$B$_3$ for instance: $R = r_0/r_1 = 0.819$ ($r_1$ is the average atomic radius of the $1^{st}$-shell atoms Co$_8$B$_3$), $R^*_{CN10} = 0.799$, thus $\Delta = 2.5 \%$. The $\Delta$ of Co$_{3}$B$_1$, Co$_{9}$B$_{3}$, Co$_{4}$B$_5$ and Co$_{12}$Si are respectively 16 $\%$, -7.7 $\%$, 10.4 $\%$ and 17.1 $\%$ ($R^*_{CN10} = 0.710$, $R^*_{CN11} = 0.884$, $R^*_{CN12} = 0.902$). Small $\Delta$ indicates that Co$_B$ is packed efficiently, close to the ideal dense packing, and Co$_B$ is another relatively dense-packed cluster. From this consideration, the ternary alloy compositions obtained on the basis of the Co$_B$-related cluster lines should have high glass forming abilities as already proved in the Cu-Zr-M (M=Ag,Al,Ti), Zr-Al-Ni and Sm-Al-Co ternary systems [7].

However, the XRD results indicate that no $\phi 2$ mm BMG rods are obtained in the designed Co-B-Si basic ternary alloys. Then 4 at. $\%$ Nb is added into the ternary basic compositions and a $\phi 3$ mm BMG rod is obtained only at (Co$_{9}$B$_{3}$-Si)$_{100}$Nb$_{8}$. Co$_B$ is the most densely packed Co-B cluster. Other quaternary alloys cannot even form $\phi 2$ mm BMGs. Furthermore, the BMG-forming range of (Co$_{8}$B$_{3}$-Si)$_{100}$Nb$_{8}$ is quite narrow with $x = 4-5$ at. $\%$ only. In order to further improve the GFAs, Co is partially substituted by Fe. BMGs are formed in [Co$_{1}$Fe$_{1}$]$_{96}$B$_{3}$Si$_{8}$Nb$_{4}$ and [Co$_{1}$Fe$_{1}$]$_{96}$B$_{3}$Si$_{8}$Nb$_{4}$ ($x=0.4$, 0.5) which are based both on quaternary (Co$_{8}$B$_{3}$-Si)$_{96}$Nb$_{8}$ and (Co$_{8}$B$_{3}$-Si)$_{96}$Nb$_{8}$. Note that the latter quaternary alloy, being based on less dense-packed cluster Co$_B$ is not BMG forming. Due to the small negative enthalpy of mixing ($\Delta H_{Co-Fe} = -1$ kJ/mol [11]) and similar atomic sizes between Co and Fe, Fe can substitute Co in the $1^{st}$-shell of a cluster to form (Co$_{Fe}$)$_{8}$B$_{3}$ or (Co$_{Fe}$)$_{8}$B$_{3}$. The significant increase in GFAs by the substitution coincides with the confusion principle [4]. Therefore, in multi-component alloy systems, the combination of the cluster line approach, minor alloying principle, and eventually confusion principle can be used to determine the good BMG compositions.

### Table 1. Experimental data of the Co-based BMGs.

| No. | Experimental BMGs (at.$\%$) | $T_g$ (K) | $T_x$ (K) | $T_m$ (K) | $T_l/T_l$ | $t$ (mm) | $I_c$ (T) | $H_c$ (A/m) |
|-----|-----------------------------|----------|----------|----------|----------|---------|---------|-----------|
| 1   | (Co$_{8}$B$_{3}$-Si)$_{96}$Nb$_{8}$, Co$_{9}$B$_{3}$Si$_{10}$Nb$_{8}$ | 861      | 895      | 1304     | 1437     | 0.599   | 0.389   | -         |
| 2   | (Co$_{8}$B$_{3}$-Si)$_{96}$Nb$_{8}$, Co$_{9}$B$_{3}$Si$_{10}$Nb$_{8}$ | 867      | 899      | 1298     | 1421     | 0.610   | 0.393   | -         |
| 3   | [(Co$_{8}$,Fe$_{1}$)$_{96}$B$_{3}$Si$_{8}$Nb$_{4}$, Co$_{9}$,Fe$_{1}$]$_{100}$Nb$_{8}$ | 869      | 915      | 1303     | 1453     | 0.598   | 0.394   | 17        | 0.90      | 5.7      |
| 4   | [(Co$_{8}$,Fe$_{1}$)$_{96}$B$_{3}$Si$_{8}$Nb$_{4}$, Co$_{9}$,Fe$_{1}$]$_{100}$Nb$_{8}$ | 871      | 926      | 1310     | 1473     | 0.591   | 0.395   | 8         | 0.88      | 3.8      |
| 5   | [(Co$_{8}$,Fe$_{1}$)$_{96}$B$_{3}$Si$_{8}$Nb$_{4}$, Co$_{9}$,Fe$_{1}$]$_{100}$Nb$_{8}$ | 859      | 901      | 1305     | 1420     | 0.601   | 0.394   | 15        | 0.94      | 3.0      |
| 6   | [(Co$_{8}$,Fe$_{1}$)$_{96}$B$_{3}$Si$_{8}$Nb$_{4}$, Co$_{9}$,Fe$_{1}$]$_{100}$Nb$_{8}$ | 856      | 902      | 1310     | 1398     | 0.612   | 0.400   | 18        | 0.98      | 4.9      |

The glass transition temperature ($T_g$), the onset temperature of crystallization ($T_x$), the onset temperature of melting ($T_m$) and the liquidus temperature ($T_l$) of the Co-based BMGs measured from DSC and DTA traces are listed in table 1. These BMGs have not only large $T_g$ or $T_x$ values, and hence high thermal stabilities, but also large thermal GFA indicators $T_g/T_l$ and $\gamma (\gamma = T_g/(T_g+T_l))$ [14]. The thicknesses ($t$) of $\phi 3$ mm amorphous alloy rods are also measured (see in table 1). A high $T_g/T_l$ or $\gamma$ value generally corresponds to a large thickness $t$ of the BMG rod, which indicates that the GFA indicators are consistent with the real BMG sizes $t$. Among them, the quinary BMGs [(Co$_{8}$,Fe$_{1}$)$_{96}$B$_{3}$-Si$_{8}$]$_{96}$Nb$_{8}$ and [(Co$_{8}$,Fe$_{1}$)$_{96}$B$_{3}$-Si$_{8}$]$_{96}$Nb$_{8}$ have the largest GFAs. In addition, the magnetic properties of these Co-based BMGs are measured and the experimental results indicate that the Co-B-Si-Nb
quaternary BMGs have no soft magnetic properties, while the quinary Co-Fe-B-Si-Nb BMGs by Fe substitution for Co exhibit good soft magnetic properties with high $I_s$ up to 0.98 T, and low $H_s$, below 6 A/m (table 1).

In our previous study on a series of Cu-Zr based ternary BMGs, we proposed an amorphous structural model in terms of dense-packed icosahedral cluster $\text{Cu}_3\text{Zr}_5$ and glue atoms for BMGs [5]. Ternary optimum BMG compositions based on this icosahedron can be roughly expressed as one $\text{Cu}_3\text{Zr}_5$ cluster plus one glue atom M, i.e. $\text{Cu}_3\text{Zr}_5\text{M}_1$, M representing a third element Al, Ag, Ti. Similarly, in the present Co-based BMGs, the basic cluster favoring glass formation is dense-packed $\text{Co}_6\text{B}_3$. The quaternary BMG composition ($\text{Co}_8\text{B}_3\text{Si}_3\text{Nb}_3$) ($\text{Co}_{0.8}\text{B}_{25.7}\text{Si}_{5.5}\text{Nb}_4$) can be understood like this: Si and Nb act as one glue atom M linking one $\text{Co}_6\text{B}_3$ cluster so that the BMG composition is expressed as $\text{Co}_8\text{B}_3\text{M} = \text{Co}_{0.8}\text{B}_{25.7}\text{M}_{6.3}$, which quite nicely agrees with experimental $\text{Co}_{0.8}\text{B}_{25.7}\text{M}_{6.5}$. And another quaternary BMG composition ($\text{Co}_8\text{B}_3\text{Si}_3\text{Nb}_3$) is also near the $\text{Co}_6\text{B}_3\text{M}$.

Our cluster line approach supports the cluster compact arrangement proposed by Miracle: dense-packed clusters centered by primary solute atoms are packed in close packed fcc-like structures and the secondary solute atoms (or glue atoms as we call them) are located in the octahedral interstitial sites [13]. For an fcc structure, the ratio of the number of lattice points to that of octahedral interstices is 1:1, which coincides exactly with the above BMG composition formula (cluster)$\text{(glue atom)}_1$.

5. Conclusions
A series of Co (-Fe)-Si-B-Nb bulk metallic glasses are obtained by using cluster line approach and minor-alloying principle. The ternary basic Co-Si-B compositions are determined by the intersection points of cluster lines. Then 4-5 at. % Nb additions into the basic composition $\text{Co}_{0.8}\text{B}_{25.7}\text{Si}_{5.5}$ derived from the most dense-packed cluster $\text{Co}_6\text{B}_3$ form quaternary bulk metallic glasses, which are all approximately expressed into a unified composition formula ($\text{Co}_{0.8}\text{B}_3$)$\text{(Si,Nb)}$. A quantity of Fe substitution for Co further improves the glass forming abilities of alloys. The typical good bulk metallic glass formers are quaternary ($\text{Co}_{0.8}\text{B}_3\text{Si}_3\text{Nb}_3$), quinary $[(\text{Co}_{0.6}\text{Fe}_{0.4})\text{B}_3\text{Si}_3\text{Nb}_3]$ and $[(\text{Co}_{0.5}\text{Fe}_{0.5})\text{B}_3\text{Si}_3\text{Nb}_3]$. The Co-Fe-based bulk metallic glasses have also good soft magnetic properties with high $I_s$ up to 0.98T, and low $H_s$, below 6 A/m.

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References
[1] Inoue A, Shen B L and Takeuchi A 2006 Mater. Trans. JIM 47 1275
[2] Chang C T, Shen B L and Inoue A 2006 Appl. Phys. Lett. 88 011901
[3] Inoue A and Takeuchi A 2002 Mater. Trans. JIM 43 1892
[4] Greer A L 1995 Science 267 1947
[5] Ma D, Tan H, Zhang Y and Li Y 2003 Mater. Trans. JIM 51 4551
[6] Xia J H, Qiang J B, Wang Y M, Wang Q and Dong C 2006 Appl. Phys. Lett. 88 101907
[7] Dong C, Wang Q, Qiang J B, Wang Y M, Jiang N, Han G, Li Y H and Wu J 2007 J. Phys. D: Appl. Phys. 40 R1
[8] Wang Q, Dong C, Qiang J B and Wang Y M 2007 Mater. Sci. Eng. A 449-451 18
[9] Wu J, Wang Q, Qiang J B, Chen F, Dong C, Wang Y M and Shek C H 2007 J. Mater. Res. 22 573
[10] Lu Z P and Liu C T 2004 J. Mater. Sci. 39 3965
[11] Boer de F R and Pettifor D G 1989 Cohesion in metals and transition metal alloys (Amsterdam: North Holland) p 167
[12] Gaskell P H 1983 Models for the structure of amorphous metals (Berlin: Springer) p 5
[13] Miracle D B 2006 Acta Mater. 54 4317
[14] Lu Z P and Liu C T 2002 Acta Mater. 50 3501