



JOURNAL OF
SYNCHROTRON
RADIATION

Volume 28 (2021)

Supporting information for article:

Local Structure Investigation of Co-Fe-Si-B Ribbons by Extended X-ray Absorption Fine Structure Spectroscopy

A. A. Deshmukh, A. P. Srivastava, J. P. Singh, Manish Kumar, K. H. Chae, K. Asokan and U. A. Palikundwar

Local Structure Investigation of Co–Fe–Si–B Ribbons by Extended X–ray Absorption Fine Structure Spectroscopy

S1. Thermodynamic and Topological Parameters

S1.1. Configurational Entropy (ΔS_c):

As configurational entropy (S_c) depends only on atomic fraction of individual constituting element and independent of the alloy system, it can be obtained by the following equation (1) [1].

$$S_c = -R \sum_{i=1}^n C_i \ln C_i \dots \dots \dots (1)$$

Here, R represents Universal gas constant and C_i is the atomic fraction of i^{th} element.

S1.2. Mismatch Entropy (ΔS_σ):

The presence of atomic disorder is calculated by the mismatch entropy term (S_σ) given in the following equation (2) [1].

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

Where, k_B is the Boltzmann's constant and parameter ζ is defined as $\zeta = \frac{1}{(1-\xi)}$. The parameter ξ is taken as 0.64 [1]. The summation of the dimensionless parameters y_1 , y_2 and y_3 is always unity and can be calculated according to following equations.

$$y_1 = \frac{1}{\sigma^3} \sum_{j \geq i=1}^n (d_i + d_j)(d_i - d_j)^2 C_i C_j \dots \dots (3)$$

$$y_2 = \frac{\sigma^2}{(\sigma^3)^2} \sum_{j \geq i=1}^n (d_i d_j (d_i - d_j)^2 C_i C_j) \dots \dots (4)$$

$$y_3 = \frac{(\sigma^2)^3}{(\sigma^3)^2} \dots \dots \dots (5)$$

$$\sigma^k = \sum_{i=1}^n C_i d_i^k \quad (k=2, 3) \dots \dots \dots (6)$$

In the above equations d_i and d_j are the atomic diameters of i^{th} and j^{th} elements [2]. Similarly, C_i and C_j are the at.% of i^{th} and j^{th} elements, respectively.

S1.3. Enthalpy of Chemical Mixing (ΔH_{alloy}^{mix}):

Extended sub-regular solution model [3] has been used to calculate enthalpy of mixing (ΔH_{alloy}^{mix}) due to the binary interactions of constituting species. It is given by the equation (7).

$$\Delta H_{alloy}^{mix} = \sum_{\substack{i=1 \\ i \neq j}}^{C_n^2} \Delta H_{C_i C_j}^{mix} \dots \dots \dots (7)$$

Where,

$$\Delta H_{C_i C_j}^{mix} = 4 \left(\sum_{k=0}^3 \Omega_k (C_{i,nor} - C_{j,nor})^k \right) C_i C_j \dots \dots (8)$$

$$C_{i,nor} = \frac{C_i}{C_i + C_j} \text{ and } C_{j,nor} = \frac{C_j}{C_i + C_j} \dots \dots \dots (9)$$

In the above equations, C_i and C_j are the concentration of i^{th} and j^{th} element. $C_{i,nor}$ and $C_{j,nor}$ are the normalized fraction of C_i and C_j , respectively. It is also important to note that $\Omega_0 = \Delta H^{mix}$ at $A_{0.50}B_{0.50}$ in an A–B alloy.

S1.4. The P_{HSS} parameter [4]:

It was noticed that the P_{HS} [5] parameter reflects the effects of enthalpy of mixing as well as atomic size mismatch for describing the GFA of the ternary alloys. Most of the stable and large dimension BMG alloys contain more than three elements. Therefore, there is a possibility that most of these elements can be chemically and topologically identical in characteristics. In such case, the P_{HS} may not sufficient parameter to define GFA in such alloys. Therefore, Rao *et al.* [4] have brought the effect of an increasing number of components into the criteria by multiplying P_{HS} with the configurational entropy normalized by R (i.e. $\Delta S_C/R$). As some quaternary and quinary alloys are also considered in the present investigation, therefore this parameter is taken into account. It can be obtained by the following Eq.10.

$$P_{HSS} = \Delta H_{alloy}^{mix} * \frac{S_\sigma}{k_B} * \frac{\Delta S_C}{R} \frac{kJ}{mol} \dots \dots \dots (10).$$

S2. Atomic Size Difference (δ):

It has been reported that the large atomic size difference could cause lattice distortion in an alloy and the corresponding strain energy could increase [6, 7]. Hence, the large atomic size differences could result in the increase of free energy in alloy which could lower the stability of solid–solution [6, 7]. On the other hand, a significant difference in atomic size ratios could lead to the sluggish diffusion of atoms in the matrix which lowers the phase transformation rate and makes the atoms segregate in the alloy, even causes nanocrystalline and glassy structures to form [6, 7]. Therefore, to describe the comprehensive effect of the atomic size difference in n–element alloy, the parameter δ is expressed as follows [6, 7]:

$$\delta = 100 * \sqrt{\sum_{i=1}^n C_i (1 - r_i/\bar{r})^2} \dots \dots \dots (11)$$

$$\bar{r} = \sum_{i=1}^n C_i r_i \dots\dots\dots(12)$$

where r_i is the atomic radius of the i^{th} element [7], C_i is the atomic fraction of the i^{th} element and \bar{r} is the average atomic radius of all elements in an alloy.

References:

1. A. Khond, D. A. Babu, S. Smaran, A. Deshmukh, B. Majumdar, J. Bhatt, and A. K. Srivastav. Thermodynamic calculation and experimental validation of Hf-rich glass forming compositions in Hf-Cu-Ni system. *J. Non-Cryst. Solids* 500, 191–195 (2018). <https://doi.org/10.1016/j.jnoncrysol.2018.07.070>.
2. G. Sheng, C. T. Liu. Phase stability in high entropy alloys: Formation of solid-solution phase or amorphous phase. *Prog. Nat. Sci. Mater. Int.* 21 (2011) 433–446. [https://doi.org/10.1016/S1002-0071\(12\)60080-X](https://doi.org/10.1016/S1002-0071(12)60080-X).
3. L. J. Gallego, J. A. Somoza, and J. A. Alonso. Glass formation in ternary transition metal alloys. *J. Phys. Condens. Matter.* 2, 6245–6250 (1990). <https://doi.org/10.1088/0953-8984/2/29/001>.
4. B. R. Rao, M. Srinivas, A. K. Shah, A. S. Gandhi, B. S. Murty. A new thermodynamic parameter to predict glass forming ability in iron-based multi-component systems containing zirconium. *Intermetallics* 35 (2013) 73. <https://doi.org/10.1016/j.intermet.2012.11.020>.
5. J. Bhatt, J. Wu, J. Xia, Q. Wang, D. Chuang, B. S. Murty. Optimization of bulk metallic glass forming compositions in Zr-Cu-Al system by thermodynamic modelling. *Intermetallics* 15 (2007) 716. <https://doi.org/10.1016/j.intermet.2006.10.018>.
6. Zhang Y, Zhou YJ, Lin JP, Chen GL, Liaw PK (2008) Solid-solution phase formation rules for multi-component alloys. *Adv. Eng. Mater.* 10:534–538. <https://doi.org/10.1002/adem.200700240>.
7. Guo S, Liu CT (2011) Phase stability in high entropy alloys: formation of solid-solution phase or amorphous phase. *Prog. Nat. Sci. Mater. Inter.* 21:433–446. [https://doi.org/10.1016/S1002-0071\(12\)60080-X](https://doi.org/10.1016/S1002-0071(12)60080-X).