Glass Transition Kinetics of 2714A amorphous alloy

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Abstract. The present study is related to the kinetics of onset crystallization, \( T_x \) and peak crystallization \( T_p \) of cobalt based metallic glass 2714A (Co65Si15B14Fe4Ni2) using Differential Scanning Calorimetry (DSC). Non-isothermal measurements were performed at different heating rates (2, 4, 6, 8 and 10 K/min). The experimental results of the crystallization were studied by two most frequently used methods, i.e., Moynihan and Kissinger. The onset crystallization was also studied by VFT and Lasock’s approaches in addition to the above two methods. The activation energy of crystallization \( E_c \) was found to be 622.86 and 638.28 kJ/mol and \( E_x \) the activation energy of onset crystallization to be 676.34 and 688.93 kJ/mol respectively. Here \( T_x \) is used as a substitution of \( T_g \) to calculate the fragility index \( m \) of the cobalt based metallic glass in the absence of \( T_g \). The fragility index, \( m \) which is a measure of glass forming ability (GFA) is also calculated and the value falls between 20 and 60. This indicates the studied metallic glass is an intermediate strong glass.

1. Introduction
In recent times, there is a renewed interest of nanocrystallite phases exhibited by metallic glasses. Yozhizawa et al first described nano-crystallization in Fe-Si-B-Nb-Cu system [1] and this work accelerated research in metallic glasses doped with transition metal. Magnetic properties may be deteriorated or enhanced due to the crystallization phase and is reported [2]. So, it is imperative to understand the microstructure and crystallization behavior. Keeping in mind, glass transition kinetics of 2714A (Co65Si15B14Fe4Ni2) which is a Cobalt based metallic glass is studied. 2714A is widely used in high frequency electromagnetic devices, soft magnetic applications and as stress sensors [3, 4].

The concept of fragility is originally introduced by Angell [5]. According to his concept; glass forming liquids are classified into three categories. The first category is strong glass formers, which obey an Arrhenian behaviour in the Angell plot and the second category is fragile glass formers and are viscosity dependent. These are studied by Vogel-Fulcher-Tammann (VFT) relation and the third category are intermediate glass formers and lie between the first and the second categories [6]. The fragility graphs are generally evaluated using viscosity data. However, \( T_g \) dependent on heating rate, measured by differential scanning calorimetry (DSC) can also be adequately exploited to understand the fragility.

The current research reports the glass transition kinetics of 2714A. Kissinger [7], and Moynihan [8]. Methods are used to fine the activation energy of crystallization (\( E_c \)) and activation energy of onset crystallization (\( E_x \)).
2. Experimental Methods
Specimens of amorphous 2714A (Co$_{65}$Si$_{15}$B$_{14}$Fe$_{4}$Ni$_{2}$) ribbons were procured from Metglas, USA. DSC measurements were performed for the as-quenched samples using Mettler Toledo instrument (Temperature precision: ±0.02 °C, energy sensitivity: better than 0.1 μW). Non-isothermal DSC curves were obtained with selected heating rates 2, 4, 6, 8 and 10 K/min$^{-1}$ from room temperature to 600 °C in air.

3. Results and discussion
The DSC thermograms of 2714A (Co$_{65}$Si$_{15}$B$_{14}$Fe$_{4}$Ni$_{2}$) amorphous alloy at different heating rates have a single exothermic peak in the temperature scanned, and an extended supercooled liquid region before the onset of the crystallization. The onset and peak temperatures ($T_x$ and $T_p$) for crystallization, are given in the Table 1. It is noticed that the $T_p$ shifted to high temperatures with increasing heating rate. This indicates that the crystallization behaves in a marked kinetic feature. This shift in the peak forms the basis for determination of the activation energy. Four different independent approaches are used to calculate the fragility index $m$ and these are discussed in detail below. Here $T_x$ is used as a substitution of $T_g$ to calculate $m$ in the absence of $T_g$.

| Heating rate (K/min) | $T_x$ (K) | $T_p$ (K) |
|---------------------|----------|----------|
| 2                   | 810.89   | 811.55   |
| 4                   | 814.46   | 816.21   |
| 6                   | 818.24   | 820.28   |
| 8                   | 821.44   | 823.07   |
| 10                  | 823.29   | 825.46   |

3.1 Kissinger procedure
Kissinger’s approach to determine $T_p$ and $T_x$ are

$$\ln (\beta / T_p^2) = -E_c / R T_p + \text{const}$$

and

$$\ln (\beta / T_x^2) = -E_x / R T_x + \text{const}$$ (1)

Where $\beta$ is heating rate and $R$ is the universal gas constant. Figures 1 and 2 shows $\ln(\beta / T_p^2)$ vs 1000/$T_p$ and $\ln(\beta / T_x^2)$ vs 1000/$T_x$ plots. The values of $E_c$ and $E_x$ are obtained from the slopes and are 622.65 and 675.34 kJ/mol.

3.2 Moynihan method
The equation of Moynihan to determine $E_c$ and $E_x$ are

$$\ln \beta = -E_c / R T_p + \text{const} \quad \text{and} \quad \ln \beta = -E_x / R T_x + \text{const}$$ (2)

Figures 1 and 2 show the graphs $\ln \beta$ versus 1000/$T_p$ and $\ln \beta$ versus 1000/$T_x$. The values of $E_c$ and $E_x$ are obtained from the slopes and are 636.26 and 688.93 kJ/mol.

The fragility index, $m$ is estimated using the relation [9]

$$r = 0.99485$$

$E_c = 622.65 \text{ kJ/mol}$

$E_x = 675.34 \text{ kJ/mol}$

$E_c = 636.26 \text{ kJ/mol}$

$E_x = 688.93 \text{ kJ/mol}$
\[ m = \frac{E_x}{2.303 RT_x} \quad (3) \]

Where \( E_x \) is activation energy for onset crystallization and \( R \) is a gas constant. The \( E_x \) is determined from the above two methods.

### 3.3 VFT fitting method

The dependence of the \( T_x \) with \( \beta \) in DSC scans is given in terms of VFT equation [10-12]

\[ B (T_x) = C \exp \left[ \frac{B}{(T_0 - T_x)} \right] \quad (4) \]

Here \( C, B \) and \( T_0 \) are adjustable VFT parameters and \( T_0 \) is called Vogel temperature or the ideal glass transition temperature. This is generally approximated to the asymptotic value of \( T_x \), at the limit of infinitely slow cooling rate. \( C \) has the dimensions of heating rate and \( B = D T_0 \), where \( D \) is called the strength parameter. The equation 4 is written as

\[ \ln \beta (T_x) = \ln C - \frac{B}{(T_x - T_0)} \quad (5) \]

The fragility index \( m \) at a particular \( T_x \) can be calculated from the equation 6, [13]

\[ m = \frac{B T_x}{2.303 (T_x - T_0)^2} \quad (6) \]

From equation 6, the value of \( m \) depends on the value of \( T_x \). Inserting \( T_x \) and adjusting \( T_0 \) value (by checking maximum regression value), plotting \( \ln \beta \) versus \( 1/(T_x - T_0) \), the slope \( B \) is determined (figure 3). Hence, substituting the \( B \) value in equation 6, the fragility index \( m \) is calculated. The \( m \) values are tabulated for the 2714A in the Table 2. The constant \( B \) and characteristic temperature \( T_0 \) are 62.143 and 794 K.

### 3.4 Lasocka’s method

The onset crystallization temperature, \( T_x \) as a function of heating rate is given by Lasocka’s empirical relation [14].

\[ T_x = A + E \ln \beta \quad (7) \]

Where \( A \) and \( E \) are empirical constants. Extrapolating the data to \( \beta = 1 \) K/min, it is possible to obtain a tentative value \( A = T_0 \), which may be the lower limit of \( T_x \) [18]. Plotting \( T_x \) against \( \ln \beta \), the value \( A = T_0 \) is obtained (figure 4). Inserting this \( T_0 \) value in equation 4, the slope \( B \) is obtained. The constant \( B \) and characteristic temperature \( T_0 \) are 14.289 and 804.69 K. Substituting \( B \) value in equation 5 the \( m \) values are determined. The \( m \) values are tabulated for 2714A in the Table 2.

![Figure 3. Plot of VFT and Lasocka](image1)

![Figure 4. \( T_x \) as a function of \( \ln \beta \)](image2)

### Table 2. Fragility index, \( m \) for 2714A.

| Heating rate (K/min) | \( T_x \) (K) | VFT | \( m \) for 2714A |
|----------------------|--------------|-----|-----------------|
| 2                    | 810.89       | 76.70 | 130.88 | 43.50 | 44.37 |
| 4                    | **814.46**   | **52.50** | **52.94** | **43.31** | **44.18** |
| 6                    | 818.44       | 37.58 | 27.65 | 43.11 | 43.97 |
| 8                    | 821.44       | 29.44 | 18.17 | 42.94 | 43.80 |
| 10                   | 823.29       | 25.89 | 14.76 | 42.84 | 43.70 |

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4. Conclusion
The high value of activation energy of crystallization indicates that the studied amorphous metallic glass is more thermally stable. It is also evident that the fragility of the metallic glass is linked to activation energy of crystallization. The value is nearly 48 and according to the Angell’s approach indicates an intermediate strong glass. The fragility index, \( m \) is calculated from \( E_x \), the activation energy of onset crystallization. The value is nearly 48 and according to the Angell’s approach indicates an intermediate strong glass. The fragility index, \( m \) shows nearly constant by all the utilized methods at heating rate 4 K/min i.e., at \( T_x = 814.46 \) K. The fragility index, \( m \) decreases with \( T_x \) and \( T_x/E_x \) in metallic glasses (figures 5 and 6). Based on the plots of figures 5 and 6 the authors proposes a relationship between \( T_x \) and \( E_x \): \( m \propto E_x/T_x \). The relation \( m \propto (E_x/T_x)^{1/3} \) shows strong dependence in polymers. This tendency is attributed to the large molecular weight of the polymers [16, 17].

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