Crystallization kinetics of Fe based amorphous alloy

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Abstract. Differential Scanning Calorimetry (DSC) experimental data under non-isothermal conditions for Fe based Metglas 2605SA1 (wt% Fe=85-95, Si=5-10, B=1-5) metallic glass ribbons are reported and discussed. The DSC Scans performed at different heating rates showed two step crystallization processes and are interpreted in terms of different models like Kissinger, Ozawa, Boswell, Augis & Bennett and Gao & Wang. From the heating rate dependence of the onset temperature (T_o) and the crystallization peak temperature (T_p), the kinetic triplet, activation energy of crystallization (E), Avrami exponent (n) and the frequency factor (A) are determined. The determined E for peak I is 354.5 ± 2.5 kJ/mol and for the peak II is 348.2 ± 2.2 kJ/mol, respectively. The frequency factor for peak I is $1.1 \times 10^{23}$ sec$^{-1}$ and for peak II is $6.1 \times 10^{20}$ sec$^{-1}$.

1. Introduction

Metallic glasses are amorphous metals. In recent times these materials are known for their high technological applications in various areas. One of the powerful and less cumbersome methods to study the crystallization kinetics in these materials is DSC. Isothermal and non-isothermal methods are utilised in DSC [1-5]. In isothermal method the sample is brought quickly near the glass transition temperature (T_g) and the heat liberated is recorded as a function of temperature, whereas in non-isothermal method the sample is heated with a constant heating rate and the heat evolved is measured as a function of temperature or time. The disadvantage of the isothermal process is to reach the required T_g and record the heat evolved at this point. This disadvantage is removed in non-isothermal method and hence the method is more favoured [6].

The present investigation is aimed at determining the activation energy of crystallization, E, Frequency factor, A and the Avrami exponent, n for the metallic glass 2605SA1 using different methods under non-isothermal conditions.

2. Experimental methods

The Fe-based amorphous alloy 2605SA1 was obtained from Metglas Inc. Co., USA as a gift. The amorphous nature of the sample is confirmed by XRD (figure 1). As-quenched samples were heated in DSC (Mettler Toledo) at five linear heating rates (2, 4, 6, 8 and 10 Kmin$^{-1}$) from RT to 840 K in air. The DSC scans were recorded by a thermal analyzer interfaced to a computer.
3. Results and discussion

The DSC thermograms of 2605SA1 alloy at different heating rates are shown in Figure 2. \( T_0 \) and \( T_p \) are given for the peak I & II in the Table 1. It is noticed that the \( T_p \) shifted to high temperatures with increasing heating rate. This shift in the peak forms the basis for determination of the activation energy, \( E \). Due to increase in the sensitivity, the peak height also increases with increasing heating rate. The non-isothermal crystallization data of DSC have been analyzed using different models as discussed below.

Table 1. Onset and peak crystallization temperatures for peak I & II

| Heating rate (K/min) | Peak I       | Peak II      |
|----------------------|--------------|--------------|
|                      | \( T_0 \) (K) | \( T_p \) (K) | \( T_0 \) (K) | \( T_p \) (K) |
| 2                    | 753.14       | 760.71       | 786.64       | 798.88       |
| 4                    | 761.16       | 769.42       | 797.54       | 809.04       |
| 6                    | 763.60       | 773.99       | 803.56       | 814.71       |
| 8                    | 766.56       | 778.24       | 804.84       | 818.43       |
| 10                   | 771.16       | 781.49       | 807.89       | 823.02       |

3.1 Kissinger method. Using Kissinger’s equation [7]

\[
\ln \left( \frac{\beta}{T_p^2} \right) = -\frac{E}{RT_p} + \ln \left( \frac{A}{R} \right)
\]  

Where \( \beta \) is the heating rate and \( R \) is the universal gas constant, the value of \( E \) can be obtained from the heating rate dependence of the peak temperature of crystallization. Figure 3 shows \( \ln(\beta / T_p^2) \) vs 1000/\( T_p \) relationship for peak I & II. The value of \( E \) for crystallization and the frequency factor (A) are obtained from the slope and intercept of the plot and are given in the Table 2 respectively.

3.2 Ozawa method. According to Ozawa [8], the change of \( \ln(1/T_p^2) \) with \( \beta \) is negligibly small compared to the change of \( \ln(\beta) \) and therefore, the Kissinger’s equation can be written as

\[
\ln \beta = -1.0516 \ \frac{E}{R T_p} + \text{const}
\]  

Plotting \( \ln \beta \) vs 1000/\( T_p \), \( E \) is calculated for peak I & II (Table 2).

3.3 Bosewell method. In order to determine the activation energy Bosewell [9] uses the following equation

\[
\ln \left( \frac{\beta}{T_p} \right) = -\frac{E}{RT_p} + \text{const}
\]  

The slope of the graph for peak I & II gives the \( E \) and are given in Table 2.

3.4 Augis and Bennett method. The equation given by Augis and Bennett[10] is
\[ \ln \left( \frac{\beta}{(T_p - T_o)} \right) = - \frac{E}{RT_p} + \ln A \]  
\hspace{1cm} (4)

Where \( T_p \) and \( T_o \) are the peak and the onset crystallization temperature respectively. Figure 4 shows the plot \( \ln(\beta/(T_p-T_o)) \) vs 1000/T\(_p\) for peak I & II and gives the \( E \) and \( A \) values for crystallization and are given in the Table 2.

3.5 Gao and Wang method [11]. This method uses the following expressions to determine the \( E \), \( A \) and Avrami exponent \( n \). The determined values are given in the Table 2.

\[ \ln \left( \frac{d\alpha}{dT} \right)_p = - \frac{E}{RT_p} + \text{const} \]  
\hspace{1cm} (5)

where \( \beta = \frac{dT}{dt} \) and \( \alpha \) is fractional crystallization.

3.6 Matusita and Sakka method. For non-isothermal data, Matusita and Sakka [12] suggested the equation

\[ \ln[-\ln(1-\alpha)] = -n \ln \beta - 1.0052 \frac{mE}{RT} + \text{const} \]  
\hspace{1cm} (6)

Here \( m \) is an integer depends on the dimensionality of the crystallization and \( n \) the Avrami exponent depends on the nucleation process. The plot \( \ln[-\ln(1-\alpha)] \) versus 1000/T\(_\alpha\) at different heating rates should give a straight line. Figure 5 shows such plot at different heating rates for peak I. Figure 6 shows the variation of \( \ln(-\ln(1-\alpha)) \) with \( \ln\beta \) at constant temperatures whose slope gives the value of \( n \). The value of \( n \) shows the scattering trend for both the peaks (Table 2).

**Figure 3** plot of \( \ln(\beta/T_p^2) \) vs 1000/T\(_p\)

**Figure 4.** plot of \( \ln(\beta/(T_p-T_0)) \) vs 1000/T\(_p\)

**Figure 5.** \( \ln[-\ln(1-\alpha)] \) vs 1000/T\(_\alpha\) at different temperatures for peak I

**Figure 6.** \( \ln[-\ln(1-\alpha)] \) vs \( \ln\beta \) at different temperatures for peak I
Table 2. Kinetic parameters obtained from different methods

| Method         | Activation energy (E) (kJ/mol) | Frequency factor (A) (Sec\(^{-1}\)) | Avrami exponent (n) |
|----------------|--------------------------------|------------------------------------|---------------------|
| Kissinger      | Peak I: 373.3±1.0, Peak II: 358.4±1.2 | Peak I: 1.1×10\(^{-23}\), Peak II: 6.1×10\(^{10}\) |                       |
| Ozawa          | Peak I: 367.0±1.0, Peak II: 353.5±1.2 | |                       |
| Bosewell       | Peak I: 379.7±1.0, Peak II: 365.2±1.2 | |                       |
| Augis & Bennett| Peak I: 289.2±2.9, Peak II: 328.2±4.6 | Peak I: 3.2×10\(^{17}\), Peak II: 8.6×10\(^{18}\) | Peak I: 4.7, Peak II: 6.2 |
| Gao & Wang     | Peak I: 363.3±6.4, Peak II: 335.9±2.9 | Peak I: 2.3×10\(^{-22}\), Peak II: 2.1×10\(^{-19}\) | Peak I: 3.8, Peak II: 5.8 |
| Matusita & Sakka| Peak I: 350.6±2.0, Peak II: 403.7±1.8 | | Peak I: 4.0, Peak II: 4.7 |

4. Conclusions
The crystallization kinetics of Fe based metallic glass, 2605SA1 have been determined under non-isothermal conditions using different methods. The obtained values of E, A and n for the peaks I & II are given in the Table 2. The E and A values by all the methods indicate consistency for both the peaks except in the case of Augis & Bennett. This discrepancy is due to the error in determining the onset temperature of crystallization. It is observed that the frequency factor is very high for both the peaks. The Avrami exponent directly reflects the mode of crystallization. The values obtained for this Fe based 2605SA1 metallic glass for the peaks I and II have a large scattering. The possible reasons may be (i) the sensitivity to alloy composition,(ii) the original state of the sample fully amorphous or partially and (iii) relaxation occurred before the crystallization. Some of these factors may also responsible for the scattering of the Avrami exponent [12] in this sample.

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