Isoconversional and Isokinetic Studies of 2605SA1 Metglass

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Abstract. Isoconversional methods (KAS, OFW, Li-Tang, and Vyazovkin) as well as isokinetic methods (IKP and CR) are used to determine the activation energy for crystallization (E), pre-exponential factor (A) and the conversion function f(α), for Fe-based 2605SA1 metallic glass. The non-isothermal differential scanning calorimetry data obtained at different heating rates ranging from 2 to 10 K/min are utilized for the analysis. The E for the peak I and II obtained by the IKP method are in good agreement with the values obtained from various isoconversional methods. The calculated kinetic triplets from IKP for peak I is: E = 445.6 ± 24 kJ/mol, A = 9.4 × 10^{22} \text{sec}^{-1} and f(α) = [-ln(1-α)]^{1/4} and for peak II is: E = 325.7 ± 8 kJ/mol, A = 7.1 × 10^{15} \text{sec}^{-1} and f(α) = α^{1/4}. All the above mentioned methods are summarized and discussed elaborately from the point of view of their applicability and correctness.

1. Introduction
The kinetic analysis of non-isothermal data (DTA, DSC etc.) is based on the rate equation [1]

\[
d\alpha/dt = k(T)f(\alpha) = A \exp(-E/RT)f(\alpha)
\]

where \( \alpha \) is the fractional crystallization in the solid reactant, A the Arrhenius pre-exponential factor, T the reactant temperature, f(\( \alpha \)) is kinetic function that depends on the reaction models, g(\( \alpha \)), E the activation energy for the reaction, and R the gas constant. When the \( \alpha \) is constant, for different heating rates \( \beta \), the methods are called isoconversional [2]. These methods are divided into two categories: 1. Linear isoconversional and 2. Non-linear isoconversional methods. The linear isoconversional methods again classified into two groups [3]. One group is called linear integral isoconversional methods and proposed by Kissinger-Akahira-Sunose (KAS) [4,5], Ozawa-Flynn-Wall (OFW) [6,7] and Li and Tang[8]. In these methods E values are calculated at a specific \( \alpha \). The other is called non-linear isoconversional method and is described by Vyazovkin [9] which assumes that the reaction model, g(\( \alpha \)) is independent of the \( \beta \).

The isokinetic (model fitting) analysis depends on the reaction model. Among the various methods of this type, the Coats and Redfern (CR) [10] and the invariant kinetic parameters (IKP) [11] are used. Present investigation uses isoconversional and model fitting methods to understand the crystallization kinetics of Fe-based 2605SA1 (wt% Fe=85-95, Si=5-10, B=1-5).

2. Experimental methods
The Fe-based amorphous alloy 2605SA1 was given as a gift from Metglass Inc. Co. USA. The amorphous nature is confirmed by X-ray analysis. The as-quenched samples were heated in DSC (Mettler Toledo) at 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 amorphous alloy at different \( \beta \) are shown in Figure1. All the DSC traces have double exothermic peaks in the temperature scanned. It is noticed that the \( T_p \) shifted to high...
temperatures with increasing $\beta$. This shift in the peak forms the basis for determination of $E$. Due to increase in the sensitivity, the peak height also increases with increasing $\beta$.

3.1. Isoconversional methods.

3.1(a). Linear Integral isoconversional methods.

(1). Kissinger-Akahira-Sunose (KAS) Method: The method uses the equation
\[
\ln(\beta/T^2) = \ln(AR/E g(\alpha)) – (E/RT)
\]  
Figure 2 gives local activation energy $E(\alpha)$, for the peaks I & II.

(2). Ozawa-Flynn-Wall (OFW) method: The expression utilized in this method is
\[
\ln\beta = -1.052E(\alpha)/R + \text{constant}
\]  
Figure 3 gives the slope $-1.0516 E(\alpha)/R$ from which the $E(\alpha)$ is calculated for both the peaks.

(3). Li and Tang method: Figure 4 shows the plot and the equation utilized in this method is
\[
\int_0^\alpha \ln(d\alpha/dT) d\alpha = G(\alpha) – E/R \int_0^\alpha (1/T) d\alpha
\]  

3.1(b). Non-linear integral isoconversional method (Vyazovkin method)

Vyazovkin’s method assumes the reaction model, $g(\alpha)$ is independent of $\beta$. So, at two different $\beta$ the ratio of the temperature integral $I(E, T_\alpha)$ to the heating rate $\beta$ is a constant. For a given $\alpha$ and a set of $n$ experiments performed under different $\beta$, the $E$ can be determined at any particular value of $\alpha$ by
finding the value of $E_\alpha$ for which the function
$$\sum_i \sum_j \left( \frac{E_i T_i}{E_j T_j} \right)^{\beta_i}$$
is a minimum. Using this procedure $E$’s are calculated and plotted in Figures 5 & 6.

### Figure 5
E at different $\alpha$ (peak I)

3.2. Model fitting methods

Model-free isoconversional methods provide accurate estimation of $E$ whereas these methods fail to give correct reaction model. Among the various model fitting methods, CR and IKP methods are used to study the non-isothermal crystallization kinetics.

#### 3.2 (a). Coats & Redfern (CR) method: This method uses the expression

$$\ln [g(\alpha)/T^2] = \ln \left( \frac{AR}{E} \right) - \frac{E}{RT}$$

CR method uses the above expression and the plot $\ln [g(\alpha)/T^2]$ versus $1/T$ gives $E$ and $A$ for a particular $g(\alpha)$. The method is repeated for all the $\beta$’s and for different $g(\alpha)$’s and $E$’s and $A$’s calculated and given in the Table. From the table it is clear that $E$’s and $A$’s are strongly dependent on correlation coefficient $r$. The general rule to determine $E$ is to look for the model corresponding $r_{\text{max}}$. But this corresponds to different $E$ value obtained from other methods. In such cases an $r$ value lower than $r_{\text{max}}$ gives the true kinetic model [12]. Applying this criterion for peak I, $g(\alpha) = (-\ln(1-\alpha))^{1/3}$ and for peak II, $g(\alpha) = 1/4$ are obtained.

| $g(\alpha)$ | $E$ (kJ/mol) | lnA | $r$   | $E$ (kJ/mol) | lnA | $r$   |
|------------|--------------|-----|------|--------------|-----|------|
| $(-\ln(1-\alpha))^{1/3}$ | 321.8±0.7 | 37.8±0.9 | 0.99024 | 528.8±0.4 | 67.0±0.5 | 0.99896 |
| $(-\ln(1-\alpha))^{1/3}$ | 434.0±0.9 | 55.6±1.2 | 0.99043 | 710.0±0.5 | 94.4±0.6 | 0.99897 |
| $(1-(1-\alpha)^{1/3})$ | 1175.6±3.1 | 172.3±4.1 | 0.98620 | 1916.4±2.3 | 275.8±2.8 | 0.99720 |
| $(1-(1-\alpha)^{1/3})$ | 1105.8±5.2 | 161.5±4.2 | 0.98646 | 1805.8±2.6 | 259.5±3.2 | 0.99591 |
| $\alpha^{1/4}$ | 190±0.6 | 76.8±0.7 | 0.98305 | $366.6±0.8$ | 42.1±0.1 | 0.98984 |

Table 1 Values of $E$ and $A$ obtained for various $g(\alpha)$ by CR method for peak I & II.

Boldface font indicates the most suitable model for the description of the solid state reaction.

#### 3.2 (b). The invariant kinetic parameter (IKP) method

$\ln A$ and $E$ are determined from CR method for each $\beta$ and particular $g(\alpha)$. This process is repeated for different $\beta$ and $g(\alpha)$, pairs $A_{ij}$ and $E_{ij}$ are determined. These pairs are given by the compensation effect expression [13]

$$\ln A_i = a_i + b_i E_i$$  

(6)
where $a_i$ and $b_i$ are called compensation effect parameters. Plotting $\ln A_i$ versus $E_i$, $a_i$ and $b_i$ are determined. Again plotting $a_i$ versus $b_i$, invariant activation parameters E’s and A’s are determined. These give invariant activation parameters for peak I, $E = 445.6 \pm 24$ kJ/mol, $A = 9.4 \times 10^{22}$ sec$^{-1}$ and for peak II is $E = 325.7 \pm 8$ kJ/mol and $A = 7.1 \times 10^{15}$ sec$^{-1}$.

4. Conclusions

Isoconversional methods proposed by KAS and OFW give $\alpha$ dependent E. The values of E calculated from KAS and OFW are very close to each other for both the peaks I and II. This trend is more pronounced for the peak II. The E values remains almost constant with $\alpha$ in the case of peak II and remains at 360 kJ/mol, whereas continuously decreases for the peak I from 460 to 360 kJ/mol. Crystallization Kinetics is a combined process of nucleation and growth. The higher value of E in the initial stage for both the peaks indicates the dominant nature of nucleation and the decreasing trend of E with $\alpha$ reveals the process of saturation of nucleation. That means the nucleation process takes place during the initial stage of transformation and negligible at the end. This is the reason why the isoconversional methods provide $E(\alpha)$ and reveals clearly the crystallization mechanism. The results of Li & Tang for the peak I & II remain at 320 kJ/mol. This may be due to no approximations involved in the derivation and shows clearly the dominant nature of nucleation.

The evaluated E values from CR and IKP methods are consistent with the values determined from isoconversional KAS and OFW methods for peak I and II. Our analysis concludes that the isoconversional methods gave $\alpha$ dependent E values which reflect the crystallization mechanism. On the other hand isokinetic methods gave single valued E and showed only one mechanism (reaction model) throughout the crystallization process for Fe-based 2605SA1. The present investigation showed that, even though diverse isoconversional and isokinetic methods are used, the results were consistent and complimentary to each other and the same trend is shown in other Co and Fe based metallic glasses [14, 15].

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