Non-isothermal crystallization kinetics of an intermetallic CoSn phase

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Abstract
Herein, the crystallization kinetics of the intermetallic CoSn phase, nucleated and grown in the microstructure of a binary CoSn alloy, have been reported. Differential scanning calorimetry traces under non-isothermal conditions were obtained and used to extract the activation energy ($E_a$) for the crystallization of the CoSn phase at various heating rates. The obtained values of $E_a$ were validated by the application of several isoconversion methods. The minimum value of $E_a$ was 1000 kJ mol$^{-1}$, which occurred at 853 K. The observed behavior of $E_a$ showed a strong temperature dependence, wherein it decreased with increasing temperature. This suggests that the rate constant for the crystallization of the CoSn phase is determined by the rates of two processes—nucleation and diffusion. The precise description of the crystallization process for the CoSn phase reveal that the reaction mechanism of this phase is following the first-order reaction.

1. Introduction

The study of metallic alloys and their thermodynamic features, such as precipitation from supersaturated solid solutions and crystallization of different intermetallic compounds, is one of the most active fields of research. This is primarily due to the wide applicability of this class of materials in modern technology, particularly for increasing the integration density of electronic devices. This integration requires the use of different interconnection materials. Lead-free solders, for instance, are widely used as interconnection materials in various levels of microelectronics packaging, and different metallic alloys have been used for this purpose. Eutectic and near-eutectic metallic alloys, such as Sn–Ag–Cu, Sn–Ag, and Sn–Cu, are the most favorable lead-free solder systems [1–3]. However, the most efficient and reliable systems for lead-free joints are Co-based alloys, which have been evaluated as alternative materials for the diffusion barrier layer for Cu metallization to prevent the rapid formation of intermetallic compounds (IMCs) [4–7]. The advantages of Co-based alloys stem from the electromigration resistance of the Co atoms, better thermal cycle fatigue life, and better mechanical strength of joints in comparison to Ni-based alloys atoms [5, 8, 9]. Additionally, Sn is the primary element in lead-free solders; hence, several studies on interfacial reactions in Co–Sn binary alloy systems have been performed [6, 10–12]. These studies investigated and examined the interfacial reactions between Sn–Ag solder and Ni–Co alloys [13], the interfacial reactions in the liquid/solid Sn/Ni–Co system with various Co concentrations [14], and the solid-state interfacial reactions in Sn/Ni–Co couples [7]. From these studies, it has been demonstrated that the various interfacial reactions typically result in the formation of several reaction phases, such CoSn$_2$ [13] and CoSn$_3$ [6, 12].

In the context of the aforementioned studies, it is apparent that studying the solid–solid phase transformations and crystallization reactions of different intermetallic Co–Sn compounds are integral. This importance stems from the possibility of exploring and developing strategies to control the crystallization and growth mechanisms of the observed phases. Controlling these mechanisms usually results in an improvement in the functionality and properties of the respective alloy. Different techniques have been used to study the phase transformation, crystallization kinetics, and interfacial reactions in Co–Sn alloy systems. These techniques
include x-ray diffraction (XRD) [15], differential scanning calorimetry (DSC) [15, 16], electron probe microanalysis (EPMA) [17], and atom probe tomography (APT) [18]. In addition, isoconversion methods can be used to obtain reliable and consistent kinetic information from both non-isothermal and isothermal data [19, 20]. Because both isothermal and non-isothermal precipitation kinetics play a critical role in determining an optimal pathway for achieving the desired properties, the concept of effective activation energy is essential for the precise description of the phase transformations as well as the crystallization kinetics of different intermetallic compounds. For the binary Co–Sn alloy system used in this study, it has been shown that the growth of the CoSn3 phase is linear with temperature at an activation energy of 121.1 kJ mol$^{-1}$ [17], while the activation energy of the crystallization of the CoSn powder mixture was determined to be 70 kJ mol$^{-1}$ [15].

Although investigations of the kinetics are important, few studies have been performed on the crystallization kinetics of Co–Sn alloy systems. These studies on kinetics are extremely important because they can reveal the complexity of multiple reactions, particularly when the activation energy of the crystallization of the intermetallic compound is dependent on the extent of conversion [21, 22].

In the present work, the crystallization kinetics of the reactions in the Co–Sn alloy system were investigated under non-isothermal conditions using isoconversion methods. The alloy system in this study was subjected to sufficient undercooling. Hence, a constant equilibrium concentration could be achieved, and the equilibrium concentration at the interface between different intermetallic compounds could also be estimated [23]. Therefore, applying isoconversion methods to obtain the required kinetic information was deemed reasonable [24]. Because there is a large variety of theoretical models and mathematical treatments for investigating the crystallization kinetics, the methods used in this study will be presented and explained in the next section.

### 2. Materials and methods

#### 2.1. Theoretical methods

The general equation for the transformation rate of a solid-state reaction under isothermal conditions is [21, 25, 26]:

$$\frac{d\alpha}{dt} = k(T) f(\alpha) \quad (1)$$

where $f(\alpha)$ is the reaction model and $k$ is defined as the effective overall reaction rate constant, which reflects the rate of nucleation frequency as well as the crystal growth rate. It is usually described by the Arrhenius temperature dependence [21, 25, 26]:

$$k(T) = A \exp \left( \frac{-E}{RT} \right) \quad (2)$$

where $A$ (1/s) is the frequency factor (also known as the pre-exponential), $E$ (kJ mol$^{-1}$) is the activation energy, and $R$ (J/K mol) is the universal gas constant.

The isothermal transformation rate $d\alpha/dt$ can be obtained by using equation (2) and $f(\alpha)$:

$$\frac{d\alpha}{dt} = A \exp \left( \frac{-E}{RT} \right) f(\alpha) \quad (3)$$

Under non-isothermal conditions, which correspond to a constant heat rate of $\beta = dT/dt$, equation (3) can be modified as follows:

$$\frac{d\alpha}{dT} = \frac{1}{\beta} \frac{d\alpha}{dt} = \frac{A}{\beta} \exp \left( \frac{-E}{RT} \right) f(\alpha) \quad (4)$$

In this context, it should be noted that there are a variety of theoretical methods that have been suggested for understanding the reaction models; hence, an understanding of the crystallization processes can be obtained. An outline of these methods, which have been used in this study to investigate the crystallization reaction of an important intermetallic phase in the binary Co–Sn alloy system, i.e., the CoSn phase, is described as follows.

(i) The first method used in this study is the Friedman method [27], which can be directly used from equation (3) at a specific crystallization fraction $\alpha$ as follows:

$$\ln \left( \frac{d\alpha}{dt} \right)_{\alpha,i} = \ln \left[ A_\alpha f(\alpha) \right] - \frac{E_\alpha}{RT_{\alpha,i}} \quad (5)$$

By introducing the Friedman parameter, $C_F(\alpha) = \ln \left[ A_\alpha f(\alpha) \right]$, equation (5) can be written as follows:

$$\ln \left( \frac{d\alpha}{dt} \right)_{\alpha,i} = C_F(\alpha) - \frac{E_\alpha}{RT_{\alpha,i}} \quad (6)$$

For specific $\alpha$ values and various heating rates ($\beta$), the activation energy $E_\alpha$ can be obtained from the slope
of plots of $\ln (d\alpha / dt)_{i,j}$ and $(1/T)_{i,j}$. Using equation (6) to determine the activation energy $E_\alpha$ requires at least three different heating rates.

(ii) The second method used in this study is the Kissinger–Akahira–Sunose (KAS) method [28], which is also called the generalized Kissinger method. From the derivation of equation (4), subsequent application of logarithm, and rearrangement, the determined Kissinger’s relation is

$$\ln \left( \frac{\beta_i}{T_{i,j}^3} \right) = C_k(\alpha) - \frac{E_\alpha}{RT_{i,j}}$$  \hspace{1cm} (7)

where

$$C_k(\alpha) = \ln \left[ \frac{d(\alpha) AR^2}{d\alpha E_{i,j}} \right]$$

The experimental determination of $E_\alpha$ and $C_k(\alpha)$ is similar to that determined by the Friedman method. In the KAS method, for each degree of conversion fraction $\alpha$, a plot of $\ln (\beta_i / T_{i,j}^3)$ against $1/T_{i,j}$ can be used to determine the activation energy of crystallization.

Against this method, the non-isothermal equation is

$$\ln \beta_i = \ln \left( \frac{A_i E_\alpha}{R g(\alpha)} \right) - 5.3305 - 1.052\left( \frac{E_\alpha}{RT_{i,j}} \right)$$  \hspace{1cm} (9)

By introducing the constant $C_w(\alpha) = \ln \left( \frac{A_i E_\alpha}{R g(\alpha)} \right) - 5.3305$, where $g(\alpha)$ is the integral reaction model, equation (9) can be written as

$$\ln \beta_i = C_w(\alpha) - 1.052\left( \frac{E_\alpha}{RT_{i,j}} \right)$$  \hspace{1cm} (10)

In this case, the activation energy of crystallization, $E_\alpha$, is calculated using the slope of the plot of $\ln \beta_i$ with $1/T_{i,j}$.

(iv) The fourth method used in this study to evaluate the activation energy $E_\alpha$ is the method introduced by Starink [21]. In this method, Starink deduced that the non-isothermal equation could be written as

$$\ln \left( \frac{\beta_i}{T_{i,j}^{1.92}} \right) = \ln \left( \frac{A_i R}{E_\alpha g(\alpha)} \right) - 1.0008\left( \frac{E_\alpha}{RT_{i,j}} \right)$$  \hspace{1cm} (11)

By introducing the constant $C_s(\alpha) = \ln \left( \frac{A_i R}{E_\alpha g(\alpha)} \right)$ where $g(\alpha)$ is the integral reaction model, equation (11) can be written as

$$\ln \left( \frac{\beta_i}{T_{i,j}^{1.92}} \right) = C_s(\alpha) - 1.0008\left( \frac{E_\alpha}{RT_{i,j}} \right)$$  \hspace{1cm} (12)

In this case, $E_\alpha$ is determined from the slope of the plot of $\ln (\beta_i / T_{i,j}^{1.92})$ against $1/T_{i,j}$.

(v) In isothermal experiments the integral reaction model (the reduced reaction model), $g(\alpha)$, can be obtained from equation (3), which can be written as [31]:

$$g(\alpha) = A(\alpha) \left[ \exp \left( \frac{-E}{RT} \right) \right] t$$  \hspace{1cm} (13)

By taking the logarithm and rearranging the variables, the activation energy, $E_\alpha$, required to reach a certain value of $\alpha$ at a set temperature $T_i$, can be calculated at the time, $t_{i,j}$ as:
can be calculated from the slope of the linear relationship between $g(\alpha) = \ln\left(\frac{g(\alpha)}{A_\alpha}\right)$ and $E_i/RT_i$.

An additional way of extracting the same information for the crystallization kinetics is by using the numerically reconstructed experimental kinetic function, $g(\alpha)$, calculated by using equation (13). In this case, the reduced reaction model, $g(\alpha)$, can be used to explain the kinetics of the crystallization, and thus to determine the mathematical model from those presented in table 1 in appendix [32] in order to illustrate the followed solid-state reaction model during the crystallization of the CoSn phase. This illustration can be achieved by knowing that for isothermal kinetics the reduced reaction model, $g(\alpha)$, is given by the following equation:

$$g(\alpha) = B \frac{t}{t_\alpha - 0.632}$$

where $B$ is a constant dependent on the form of the function $g(\alpha)$ and $t_\alpha$ is the time required to reach a specific volume of the crystallized fraction. The above equation is dimensionless and independent of the kinetic rate constants. The volume of the crystallized fraction $\alpha$ was chosen to be equal to 0.632, because when the reduced activation energy ($E_i/RT$) approaches infinity, the conversion fraction approaches $\alpha = 0.632$ at the corresponding temperature and $B = 1$.

As stated earlier, this study examined the crystallization kinetics behind the formation of one of the intermetallic phases in the binary Co–Sn alloy. An intermetallic phase, CoSn, was selected as a case study in the present work. This phase generally forms in the microstructure of the binary Co–Sn alloy [33] and has a 1:1 Co:Sn ratio. It has also been proven that this phase enhances the microstructural and thermally activated reactions in the Co–Sn binary system [34]. According to the binary Co–Sn phase diagram [33], the CoSn phase can be found in the microstructure of alloys with the composition Sn–25 at% Co. Thus, in the present work, a Co–Sn alloy was prepared with a 1:3 ratio of Co:Sn. The structure, morphology, and expected reaction of the CoSn phase with its crystallization kinetics were investigated using XRD, scanning electron microscopy (SEM), and DSC.

### 2.2. Sample preparation

Appropriate quantities of Sn shots with a purity of 99.9% and Co shots with a purity of 99.9% were purchased from Sigma Aldrich, mixed at a Co:Sn ratio of 1:3, and subsequently melted in an arc-melting furnace (Edmund Buhler GmbH) within a copper hearth. The sample was inverted and melted several times to completely homogenize the alloy composition. The arc-melting procedure was performed in a chamber pumped to $1 \times 10^{-3}$ Pa and backfilled with Ar gas to atmospheric pressure. The synthesized alloy was subjected to supercooling in air immediately after the melting procedure.
2.3. Instrumentation
Thermal analyses were performed using DSC with a temperature accuracy of \( \pm 0.1 \) K in a Netzsch DSC 204 F1. Samples weighing 10 mg were placed in an \( \text{Al}_2\text{O}_3 \) crucible. Non-isothermal DSC curves were obtained at heating rates of 5, 10, and 25 \( \text{K min}^{-1} \) under a dynamic \( \text{N}_2 \) atmosphere (20 ml min\(^{-1}\)). The DSC signals were recorded while heating the alloy from 298 to 973 K. Kinetics analysis of the obtained DSC thermograms was performed using the AKTS-Thermokinetics software package \(^{[35]}\).

The structure of the as-synthesized samples as well as the samples heated via the DSC at various heating rates were examined using XRD (STOE STADI MP) with a Mythen 1K silicon detector and a Cu anode producing primarily \( \text{CuK}_\alpha \) radiation. The powder diffraction data were collected between 10° and 90° to identify the intermetallic compounds in the tested alloys. The samples were previously ground with a gate mortar.

The original microstructure morphologies were investigated (without prior etching of the sample surface) via SEM (Quanta 600) and x-ray spectroscopy (EDX). The samples were prepared by mounting a piece of the sample in a goniometer holder and mechanically grinding with 800 and 1200 grit SiC paper, respectively, with distilled water. This step was followed by final polishing using colloidal silica with a particle size of 30–120 nm on a cloth to eliminate scratches. The SEM micrographs were recorded at an accelerating voltage of 30 kV using a backscattered electron detector (BSE) to reveal the compositional contrast. Chemical analysis and elemental compositions were obtained using an EDAX system (EDS Inc., Mahwah, NJ, USA) from FEI. The chemical composition of each observed phase was estimated by averaging five measurements taken at different locations in the phase, while the errors were quantified by calculating the standard deviation for the obtained values of the chemical compositions.

3. Results and discussion

3.1. Structural studies
Quantitative and qualitative estimations were performed on the as-prepared alloy to obtain a clear image of the morphology and composition of the microstructure, including the intermetallic phases present. SEM micrographs were recorded using BSE signals, and a sample SEM image is shown in figure 1. Areas of different contrast were readily observed in the SEM image, and the presence of these areas provided a strong indication of the presence of different phases in the microstructure. Using EDX analyses, the phases observed in the microstructure were identified as pure Sn (named as phase 1 in figure 1), CoSn (named as phase 2 in figure 1), and CoSn\(_3\) (named as phase 3 in figure 1). The average chemical composition of phase 1 (pure Sn) was estimated to be 99.4 \( \pm 0.8 \) at% Sn and 0.6 \( \pm 0.1 \) at% Co, while the average chemical composition of phase 2 (CoSn) was
estimated to be 52 ± 3 at% Sn and 48 ± 3 at% Co. Finally, phase 3 (CoSn$_3$)$_3$ had an estimated chemical composition of 74.85 ± 0.9 at% Sn and 25.14 ± 0.9 at% Co.

DSC measurements were conducted on the as-prepared sample to elucidate the reactions that generated the observed intermetallic phases shown in figure 1 and deduce the temperature range of the stability of these phases. The DSC signals, which were recorded by heating the alloy sample from 298 to 973 K at heating rates of 5, 10, and 25 K min$^{-1}$, exhibited a typical shape, as shown in figure 2.

The crystalline nature and the presence of various intermetallic phases in the as-prepared sample as well as in the samples that were heated using DSC at various heating rates were confirmed by XRD measurements. The XRD patterns are shown in figure 3. The XRD pattern for the respective alloy could be indexed by the CoSn, CoSn$_3$, CoSn$_3$, and Sn phases. This indexation was based on comparisons with the standard powder XRD data for the metal Sn phase (figure 3(a)), the intermetallic phase CoSn (figure 3(b)), the intermetallic phase CoSn$_3$ (figure 3(c)), and the intermetallic phase CoSn$_3$ (figure 3(d)). The as-prepared sample was mainly crystalline, with the pure Sn, CoSn, and CoSn$_3$ phases present, as shown in figure 3(e). Non-isothermal heating of the sample using DSC at a heating rate of 5 K min$^{-1}$ also revealed the presence of the Sn, CoSn, and CoSn$_3$ phases, as shown in figure 3(f).

It is worth noting that the Sn, CoSn, and CoSn$_3$ phases were observed in the XRD patterns of the samples heated using DSC at heating rates of 10 and 25 K min$^{-1}$, as shown in figures 3(g) and (h), respectively. This observation served as evidence of the presence of various intermetallic compounds in the alloy microstructure after the non-isothermal heating procedure was applied. In this context, it should be noted that the CoSn phase has a hexagonal crystal structure with a space group of P6/mmm [36], while the CoSn$_3$ phase has two crystal structures—Cmca with an orthorhombic crystal structure for the $\beta$CoSn$_3$ phase and $I_4/m$ with a tetragonal crystal structure for the $\alpha$CoSn$_3$ phase [37]. Distinguishing between the $\alpha$CoSn$_3$ and $\beta$CoSn$_3$ phases was not possible from the XRD data in figure 2 alone due to the similarity of the XRD patterns of both phases. Usually, $\alpha$CoSn$_3$ and $\beta$CoSn$_3$ phases are modeled as a single-phase as suggested by Jiang et al [38]. The CoSn$_3$ and Sn phases have a tetragonal crystal structure with a space group of $I_4/mcm$; and a body-centered tetragonal crystal structure with a space group of $I_4_1/amd$, respectively [39, 40]. From the structural analysis of the investigated alloy, solid-state phase transformations between different intermetallic phases could be clearly observed, as shown in the DSC signal in figure 2. In general, thermally activated transformation processes in solid materials can be investigated by both isothermal and non-isothermal experiments. Non-isothermal experiments at a constant heating rate are usually performed via DSC measurements. The calorimetry analysis technique allows for rapid determination of the required kinetic parameters for the observed transformations [24]. Additionally, non-isothermal experiments have several advantages, such as the rapid test speed and the ability to rate-control processes to determine the kinetic parameters [41].

Inspection of the DSC thermograms (in figure 2) revealed the presence of an exothermic peak at 473–523 K (denoted as P1), followed by an endothermic peak at 523–573 K (denoted as P2). The DSC signals also exhibited two exothermic peaks at 573–623 K (denoted as P3) and 823–853 K (denoted as P4). By comparing the DSC signals in figure 2 with the binary Co–Sn phase diagram [33] and with a basic assessment of the DSC signals obtained for a similar alloy system [42], it was concluded that peak P1 corresponded to the crystallization of the $\alpha$CoSn$_3$ phase, while peak P2 corresponded to the dissolution of this phase. Peaks P3 and P4 corresponded to the crystallization of the $\beta$CoSn$_3$ and CoSn phases, respectively. In this context, one should note that crystals of CoSn with a higher Co content than that of the Sn-rich matrix usually reacts with the pure Sn

Figure 2. DSC signal of as prepared alloy heated from 298 to 973 K at heating rates of 5, 10, and 25 K/min showing the presence of four reactions peaks.
phase, which was observed to envelope these CoSn crystals, as it can be seen in SEM micrograph in figure 1. A preictic reaction between CoSn phase and pure Sn-rich matrix is usually processed to produce the microcrystals of the CoSn$_2$ phase. Different studies [18, 43] observed that the CoSn$_2$ phase was quite thin and existed as a nanoscale thin layer. This explains the lack of this phase observed by SEM in figure 1 and from the DSC measurement in figure 2. Nevertheless, a slight indication of the presence of the CoSn$_2$ phase in XRD patterns of the samples heated using DSC at heating rates of 10 and 25 K min$^{-1}$ (figures 3g and 3h).

To examine the accuracy and the possibility of applying isoconversion methods to the metallic alloy system, the CoSn phase was selected as a case study, and the circled region surrounded the peak P4 in figure 2 shows the area of interest as illustrated in figure 4. After applying the nonlinear Gaussian curve fit to the data sets for peak 4 in figure 2 for each heating rate, the resulted peaks are shown in figure 4(a) which displays the variation in the exothermic peak P4, that corresponded to the crystallization of the CoSn phase, with temperature as well as the DSC traces of this peak at the three selected heating rates (5, 10, and 25 K min$^{-1}$). From this figure, it is evident that the peak temperature ($T_P$) shifted upward slightly with increasing heat rate. This observation can be attributed to the variation in the reaction kinetics with increasing heating rate. DSC analyses with different heating rates are required to determine the kinetic parameters because multiple scans associated with several measurements are needed [43]. Increasing the peak temperature ($T_P$) by increasing the heating rate ($\beta$) induces variation in the conversion fraction ($\alpha$) with temperature ($T$) is expected as shown in figure 5(b). The ratio between $\alpha$ and the corresponding time ($t$) yields the crystallization rate ($d\alpha/dt$); curves of the relationships between $d\alpha/dt$ and $T$ at different heating rates are shown in figure 5. Similar to figure 4(a), the peak temperature ($T_P$) as well as the crystallization rate shifted upward slightly with increasing heat rate.

Figure 3. X-ray patterns and expected peaks for (a) Sn phase. (b) CoSn phase. (c) CoSn$_3$ phase. (d) CoSn$_2$ phase. (e) As prepared alloy. (f) DSC heated sample by heating rate of 5 K min$^{-1}$. (g) DSC heated sample by heating rate of 10 K min$^{-1}$. (h) DSC heated sample by heating rate of 25 K min$^{-1}$.

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3.2. Activation energy of crystallization reaction

Thermal treatments and induced thermally activated reactions in metallic systems have considerable synthetic potential in solid-state synthesis. Thermally activated reactions obtained using different synthesis methodologies are usually associated with a reduction in the activation energy barrier for the solid-state reactions. Thus, diffusion of different reactants within the microstructure of the metallic system is expected [43].

To utilize the potential thermally activated reaction in the CoSn alloy, the activation energy of the crystallization reactions for several intermetallic phases must first be evaluated.

The first step in evaluating the activation energy of crystallization as a function of temperature for the selected phase in this study (CoSn) was applying the isoconversion methods described in equations (6), (7), (10) and (12) to the overall crystallization data to obtain the dependency of $E_a(\alpha)$ on $\alpha$; and $E_a(T)$ on $T$ as shown in figure 6. The relationship between $E_a(\alpha)$ and $\alpha$ and as well as between $E_a(\alpha)$ and the frequency factor ($\ln[A_\alpha, f(\alpha)]$) can be seen in figure 6(a). By replacing $\alpha$ with the respective temperature interval $T$, the dependency of $E_a(T)$ on $T$ can be obtained [21, 24, 44]; this relationship is shown in figure 6(b). The relationship in figure 6(b) was deduced using the Friedman and OFW methods. It is evident that the obtained results for $E_a(\alpha)$ shown in figure 6(a) were well matched with all the isoconversion methods used here, which produced identical values with a slightly lower values for the Friedman method. This shift in the obtained $E_a(\alpha)$ values when using the Friedman method was also observed in other compounds, such as Sb$_9$, Te$_{30.1}$, Se$_{70.8}$ and selenium thin films [45, 46]. The variation in $E_a(\alpha)$ with $\alpha$ can be interpreted in terms of the multi-step mechanism for the respective phase (CoSn). Moreover, the values of $E_a(\alpha)$ in figure 6(a) reveal that $E_a(\alpha)$ was a

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**Figure 4.** Variation in the exothermic peak P4 circled in figure 2. (a) The exothermic peaks traces at different heating rates. (b) Variation of the conversion fraction ($\alpha$) with temperature ($T$).

**Figure 5.** Relationships between the crystallization rate ($\Delta\alpha / \Delta t$) and temperature ($T$) at different heating rates.
obtained under non-isothermal conditions from different values for the CoSn phase. The pure Sn phase is expected when the temperature increased, the reaction progressed faster. This behavior could be observed clearly from the fast cooling of the CoSn phase. Moreover, an approach to the maximum value of conversion value at this temperature, the solid phase will get involved in a peritectic reaction with the liquid Sn melt, with a composition of 1:3 Co: Sn (the same used composition in this present study), the solidification should occur at 1238 K under equilibrium cooling condition. On further cooling, the compound CoSn will crystallize until a temperature of 844 ± 3 K is reached. At this temperature, the solid CoSn will get involved in a peritectic reaction with the liquid Sn-rich melt to form CoSn2 [43]. This reaction mainly occurs because of the reduction in the activation energy barrier, which is confirmed in figure 6(b). The induction of the solid—solid phase transformation between the CoSn and CoSn2 phases is expected when the (Ea/α) value is reduced.

After determining the kinetic parameters of the CoSn phase under non-isothermal conditions, it is possible to predict the crystallized volume fraction (α) under isothermal conditions using the AKTS-Thermokinetics software package as shown in figure 7. The relationships between α and time t under isothermal conditions at 833, 838, 843, 848, 853, and 858 K are shown in figure 7(a). The relationships between α and t were similar for all selected temperatures and proved the progress of the reaction with time at every selected temperature. Moreover, this figure reveals the deaccelerating behavior of α with increasing temperature. However, as the temperature increased, the reaction progressed faster. This behavior could be observed clearly from the fast approach to the maximum value (α = 1) at the highest temperature (858 K). By plotting ln τ0 for every specific conversion value α against 103/T K−1, various straight lines were obtained, as displayed in figure 7(b). Using equation (14), it can be stated that the slopes of the resulting straight lines corresponded to the values of Eα for every specific conversion value. These values of Eα(α) as functions of the corresponding α are shown in figure 7(c). This figure reveals that the relation between Eα(α) and α was identical to that of the non-isothermal condition shown in figure 6(a). This identity confirms the validity of the obtained Eα(α) values for the CoSn phase. Moreover, figure 6(a) reveals that the obtained value of Eα(T) was positive, exhibited a maximum at 835 K, and then decreased as the temperature increased further. This indicates that the crystallization rate increases with increasing temperature at the beginning, and then, it has been decreased as the temperature increases (see figure 5). This behavior of Eα(T) suggests that the constant rate of crystallization for the CoSn phase is determined by the rate of two processes—nucleation and diffusion. These two mechanisms are likely to have different activation energies, and thus the effective activation energy of the transformation will vary with
temperature \[48\]. Therefore, it is reasonable to assume that both mechanisms are active during the crystallization of the CoSn phase.

For the aim of the precisely description of the crystallization process, and to distinguish the suitable kinetic model from the list of the solid-state reaction models in table 1 in appendix, it will be useful to analyze the integral reaction model, \(a_g\) by using equation \((15)\). Figure 8 shows the experimental values of \(a_g\) for the peak 4 in figure 2. Plotting the numerical data of \(a_g\) versus the conversion fraction \(\alpha\) and comparing them with the theoretical models listed in table 1 is shown in figure 8 (a). In this figure, the theoretical models are represented by the solid and dashed lines, while the obtained experimental data of the \(a_g\) at different corresponded temperature are represented by several symbols. Carefully inspection of the comparison of the experimental results with those for the theoretical models can provide information about the reaction mechanisms during the formation of the respected phase. It is clearly seen in figure 8(a) that the crystallization reaction of the CoSn phase followed the first order reaction model called \((F1)\) in table 1. A specific view of the comparison between the experimental values of \(a_g\) and the solid lines calculated according to the to the nth order reaction models of F1, F1.5, F2 and F3 is shown in figure 8(b). Without a doubt, a well matching with the reaction model of F1 is clearly observed at all selected temperatures and for the whole range of the crystallization processes. Thus, it can be deduced that the crystallization mechanism of the CoSn phase is following the first-order reaction in which the reaction rate is proportional to the probability of two reactants bumping into each other \[49\]. This justification is supported by the values of the activation energies obtained from figures 6 and 7.

The present study demonstrates the ability of DSC and isoconversion methods to measure and obtain the activation energy of the intermetallic phases. This capability can be extended to other intermetallic phases and, hence, will also provide direct insights into their kinetic behavior.

4. Conclusion

By applying isoconversion methods, the activation energy of crystallization \(E_a\) of the CoSn phase in the microstructure of the binary CoSn alloy was obtained. The results show that \(E_a\) is strongly temperature
dependent and its value decreases with increasing temperature. The minimum value of $E_a$ was determined to be 1000 kJ mol$^{-1}$ at temperature of (853 K). Thus, a large reduction in the activation energy of the CoSn phase was observed. The behavior of $E_a$ with increasing temperature also demonstrated the involvement of both nucleation and diffusion mechanisms during the crystallization of this phase. The deduced reaction mechanism during the formation of the CoSn phase is following the first-order reaction in which the reaction rate is proportional to the probability of two reactants bumping into each other.

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Appendix

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