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## FROM President's Desk

Dear Members,

It gives me immense pleasure to bring out this special issue of ITAS bulletin on kinetics of thermophysical and chemical processes in condensed matter. I am thankful to Professor Arun Pratap, the Guest Editor of this issue who has spared his valuable time to collect articles from experts in this field. In his pursuit, he has been successful in receiving several articles from experts on thermoanalytical methods and kinetic investigations. The collected articles cover both fundamentals and applied aspects of the topic ranging from 'Overview of nucleation and growth mechanisms' by Dr. Radhika Barua, 'Review on Thermal characterization of Polymer nano-composites' by Professor N.S. Saxena, 'Kinetics of nano-particle catalyzed bio-mass pyrolysis' by Dr. Pritam Deb and his group, 'First order magneto-structural phase transition and its implications on the functional properties of Fe-Rh system' by Dr. Meghmalhar Manekar, and 'Kinetics of phase transformation in metallic glasses' with crystallization process by Professor Arun Pratap and his group.

I hope that our readers will find the contents quite interesting and useful and I request them to provide us feedback so as to enable us in further improving ITAS Bulletin.

This time there has been a long waiting period to bring out this issue. We regret this delay and hope for receiving articles containing recent findings on different features of thermal analysis from uprising scientists from home and abroad. Members are requested to provide their suggestions on future articles and possible contributors for enriching ITAS bulletin.

I place on record my sincere thanks to the editorial team in bringing out this issue.

Dasarathi Das

## **EDITORIAL**



Ever since I attended 34th annual session of North American Thermal Analysis Society (NATAS) at Bowling Green, Kentucky, USA in 2006 as a speaker in Special Session on Kinetics in honor of Professor Takeo Ozawa, I am highly fascinated with the various descriptions of both isothermal and non-isothermal methods of analysis. Methods of analysis of isothermal processes, e.g. Johnson-Mehl-Avrami-Kolmogrov (JMAK), have been extended to non-isothermal cases assuming certain conditions. Further, it has been always debated, whether non-isothermal methods may be appropriate for analysis of kinetics of processes involved or not. The activation energy 'E' is a very important parameter which represents the threshold of energy required to activate a process. A deeper look into the analysis methods of non-isothermal reactions gave way to two separate approaches namely, iso-kinetic and iso-conversional techniques. Iso-kinetic analysis provides single value of activation energy, 'E' for the entire process. On the contrary, iso-conversional approach indicates that the activation energy,  $E(\alpha)$  is a function of extent or degree of conversion, ' $\alpha$ '. Activation energy, 'E', derived using iso-conversional method is a signature of the varying reaction mechanism during the process of a particular reaction. There has been lot of controversy about the point whether 'E' obtained through either iso-kinetic approach or iso-conversional method is having any significance or it is just a parameter only. There is another school of thought asking questions about reproducibility on one hand and consistency of obtained values on the other. Similar type of curiosities have also been shown about frequency factor, denoted by k<sub>0</sub> or A, encountered during analysis.

Among all these speculations, questions and possible understanding, it is a pleasure to present before you, this special issue of Indian Thermal Analysis Society (ITAS) bulletin on kinetics. In my pursuit to get articles of high caliber, I contacted practicing thermal analysis scientists not only all over India but also a cross the boarder. I could get articles on both fundamentals as well as applied aspects of the topic ranging from 'Overview of nucleation and growth mechanisms' by Dr. Radhika Barua to 'Review on Thermal characterization of Polymer nano-composites' by Professor N.S. Saxena. 'Kinetics of nano-particle catalysed biomass pyrolysis' has been nicely addressed by Dr. Pritam Deb and his group using a newly proposed method of analysis developed by Deb himself. 'First order magneto-structural phase transition and its implications on the functional properties of Fe-Rh system' feature in the article by Dr. Meghmalhar Manekar through nucleation and growth dynamics. An article on 'Kinetics of phase transformation in metallic glasses' with crystallization process as an example, has been contributed from our group. The kinetics of crystallization of a multi-component metallic glass has been discussed in detail. In this article, applicability of JMAK method originally given for isothermal reactions has been checked for analyzing various steps of non-isothermal multi-step crystallization. Besides, an effort has also been made to check one-to-one correspondence between theory and experiment using master plot method and also by comparing experimentally obtained normalized heat curves with those derived using Sestak-Berggren (SB) and JMAK methods.

I hope this special issue serves the purpose as a very useful reference for practicing thermal analysts working in different fields.

Sunday, 10th August, 2014 Raksha Bandhan, Sawan Purnima Vadodara Professor Arun Pratap Guest Editor

### FUNDAMENTAL CONCEPTS OF KINETICS OF PHASE TRANSFORMATIONS: OVERVIEW OF NUCLEATION & GROWTH MECHANISMS

#### Radhika Barua

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#### 1. Introduction:

In classical thermodynamics, thermodynamic system – a phase – is characterized by a set of thermodynamic parameters associated with the system. These parameters include macroscopic properties, such as pressure (P), temperature (T), enthalpy (H) and Gibbs free energy (G). A phase transition is defined as the transformation of a thermodynamic system from one state of matter to another. For phase transformations which occur at a constant temperature and pressure, the stability of the system can be explained by the Gibbs free energy (G) - an extensive property proportional to the amount of material in the system. Mathematically, the Gibbs free energy of a system is expressed as a function of temperature and pressure:

$$G(T, P) = U + PV - TS \tag{1}$$

where T is the temperature of the system (K); P is the pressure of the system  $(N/m^2)$ ; U is the internal energy of the system (J); V is the volume of the system  $(m^3)$  and S is the entropy of the system (J/K).

An important consequence of the laws of classical thermodynamics is that at constant temperature and pressure, a closed system (i.e one of fixed mass and composition) will be in stable equilibrium if it has the lowest possible value of the Gibbs free energy (G), or in mathematical terms:

$$dG = 0 \tag{2}$$

To illustrate the definition of equilibrium graphically, a schematic representation of the variation of Gibbs free energy with the system configuration is shown in Figure 2. Configuration A here is the most stable equilibrium state. At this point, small changes in the arrangement of atoms to a first approximation produces no change in G (i.e. Eq. (2) is satisfied). Configuration B lies at a local minima in the free energy but it does not have the lowest possible value of G. It is therefore the metastable equilibrium state. Thermodynamically, any transformation that results in a decrease in Gibbs free energy is possible. Therefore, a required criterion for phase transformation is

$$\Delta G = G_2 - G_1 < 0 \tag{3}$$

where,  $G_1$  and  $G_2$  are the free energies of the initial and final states, respectively



Figure 1. Schematic representation of variation of Gibbs free energy with the arrangement of atoms. Configuration "A" has the lowest free energy and is therefore the arrangement when the system is at stable equilibrium. Configuration "B" is a metastable equilibrium. Figure adapted from [1]. It is important to note that sometimes metastable states can be very short lived; at other times they can exist almost indefinitely. Graphite and diamond are prototypical examples of stable and metastable equilibrium conditions. Given *sufficient time*, diamond at room temperature and pressure will ultimately transform to graphite. The answer to the question, "*How fast can a phase transformation proceed*", belongs to the field of kinetics of phase transformations. This article provides basic information essential for developing a comprehensive understanding of kinetics of phase transformations. To this end, it is critical to realize that a great majority of phase transformation in metals and alloys occur by a process known as *nucleation and growth*.

In this article, a basic overview of nucleation and growth mechanisms in pure metals is provided first, followed by a discussion regarding the classification of nucleation and growth transformations. From the perspective of applied science, it is essential to bear in mind that phase transformations of pure metals are rarely encountered in practice. Typically, commercially available pure metals contain impurities to change the characteristics of phase transformations from pure metal to alloy behavior. Phase transformation in binary alloys (single phase, eutectic/peritectic alloys etc) is beyond the scope of this review. More information regarding this subject is available in references [1-4]. The final section of this article provides an overview of the Johnson-Mehl-Avrami-Kolmogorov (JMAK) theory - a theoretical model used routinely to deduce the mechanism of phase transformations that occur via nucleation and growth.

## 2. Nucleation & Growth Mechanisms in Pure Solids



# Figure 2. Graphical representation of difference in free energy between liquid and solid ( $\Delta G$ ) close to the melting point (Tm). Figure adapted from[1].

In dealing with phase transformations, we are often concerned with the difference in free energy between two phases at temperatures away from the equilibrium temperature. For example, if a liquid metal is under cooled by  $\Delta T$  below its melting point  $T_m$  before it solidifies, solidification will be accompanied by a decrease in free energy  $\Delta G$ , as shown in Figure 2. This free energy provides the driving force for phase transformation (i.e. solidification in this example). Ideally, if a liquid is cooled below its equilibrium melting temperature, one would expect the liquid phase to spontaneously solidify; however, this is not always the case. For example, liquid Ni can be super cooled to 250 K below its  $T_m$  (1726 K) and held there indefinitely without any transformation occurring [1]. To understand the physical phenomena behind this observation it is important to note that phase transformation begins by formation of very small solid particles or nuclei. Normally undercoolings as large as 250 K are not observed, since in practice the walls of the liquid container and solid impurity

particles in the liquid catalyze the nucleation of solid at small undercoolings of less than 10 K. This is known as heterogeneous nucleation. Large undercoolings of 250 K as mentioned above are only obtained when no heterogeneous nucleations sites are available, *ie* is when the solid must form homogeneously from the liquid. Critical aspects and differences between homogeneous & heterogeneous nucleation are discussed below.

#### (a) Homogeneous Nucleation

Figure 3 shows a schematic representation of the process of homogeneous nucleation. Consider the phase transformation of a hypothetical system from phase  $\alpha$  to phase  $\beta$  at a temperature  $\Delta T$  below its equilibrium phase transformation temperature  $T_t$ . Mathematically, the initial free energy of the system (Figure 3(a)) is given by:

$$G_1 = (V_{\alpha} + V_{\beta})G_{\nu}^{\alpha} \tag{4}$$

Where,  $V_{\alpha} \& V_{\beta}$  is the volume of phase  $\alpha$  and  $\beta$  respectively and  $G_{\nu}^{\alpha}$  is the free energy per unit volume of phase  $\alpha$ .

If some of the atoms of phase  $\alpha$  cluster together to form phase  $\beta$  (Figure 3(b)), then the free energy of the system will change to:

$$G_2 = V_{\alpha}G_{\nu}^{\alpha} + V_{\beta}G_{\nu}^{\beta} + A_{\alpha\beta}\gamma_{\alpha\beta} \qquad (5)$$

Here,  $A_{\alpha\beta}$  and  $\gamma_{\alpha\beta}$  refers to te  $\alpha/\beta$  interfacial area and energy respectively.





## Figure 3. Schematic representation of the process of homogeneous nucleation.

From Equations (4) and (5), it may be deduced that the free energy change in the system is:

$$\Delta G = G_1 - G_2 = -V_{\beta} (G_V^{\alpha} - G_v^{\beta}) + A_{\alpha\beta} \gamma_{\alpha\beta} = -V_{\beta} \Delta G_v + A_{\alpha\beta} \gamma_{\alpha\beta}$$
(6)

Below  $T_t$ ,  $\Delta G_v$  is positive so the the free energy change associated with the formation of a small volume of phase  $\beta$  has a negative contribution, but there is also a positive contribution due to the creation of a  $\alpha/\beta$ interface. The excess free energy associated with phase  $\beta$  can be minimized by the correct choice of particle shape. If  $\gamma_{sl}$  is isotropic this is a sphere of radius *r*. Eq. (6) can then be modified to:

$$\Delta G = -\frac{4}{3}\pi r^{3}\Delta G_{v} + 4\pi r^{2} \gamma_{\alpha\beta} \qquad (7)$$

Eq. (7) is graphically represented in Figure 4.



Figure 4. Schematic representation of free energy change associated with homogeneous nucleation of sphere of radius r.

Since the interfacial term (second term in Eq. [6]) increases as  $r^2$  whereas the volume free energy term (first term in Eq. [6]) decreases as  $r^3$ , the creation of a small particles of phase  $\beta$  always leads to a free energy increase. For a given undercooling there is a certain radius  $r^*$  which is associated with a maximum excess free energy increase. If  $r < r^*$  the system can lower its free energy by dissolution of the solid, whereas when  $r > r^*$  the free energy of the system decreases if the solid grows. Unstable solid particles with  $r < r^*$  are known as clusters or embryos while stable particles with  $r > r^*$  are referred to as nuclei. Typically  $r^*$  is known as the critical nuclei size. Since dG = 0 when  $r = r^*$ , the critical nuclei is effectively in unstable equilibrium with the surrounding liquid. Mathematically, it can be shown that  $r^*$  and  $\Delta G^*$ decreases with increasing undercooling:

$$r^* = \frac{2\gamma_{\alpha\beta}}{\Delta G_v} = \left(\frac{2\gamma_{\alpha\beta}T_t}{L_v}\right)\frac{1}{\Delta T} \tag{8}$$

And

$$\Delta \boldsymbol{G}^* = \frac{16\pi\gamma_{\alpha\beta}^3}{3(\Delta \boldsymbol{G}_{\nu})^2} = \left(\frac{16\pi\gamma_{\alpha\beta}^3 T_m^3}{3L_{\nu}^3}\right) \frac{1}{(\Delta T)^3} \tag{9}$$

If the initial phase has  $C_0$  atoms per unit volume, the number of clusters that have reached the critical size for phase transformation at a given undercooling may be obtained from Eq. [10]:

$$C^* = C_0 exp\left(\frac{\Delta G_{hom}}{kT}\right) clusters m^{-3}$$
 (10)

The addition of one more atom to each of these clusters will convert them into stable nuclei and if this happens with a frequency  $f_0$ , the homogeneous nucleation rate will be given by:

$$N_{hom} = f_0 C_0 exp\left(-\frac{\Delta G_{hom}^*}{kT}\right) nuclei m^{-3} s^{-1} \quad (11)$$

Where,  $f_0$  is a complex function that depends on the vibration frequency of the atoms, the activation

energy for diffusion in the liquid and the surface area of the critical nuclei. In a practical scenario, homogeneous nucleation during a phase transformation is never observed. Instead heterogeneous nucleation occurs at crevices in mould walls or at impurity particles suspended in the liquid.

#### (b) Heterogeneous Nucleation

To explain the physical principle behind heterogeneous nucleation, Figure 5 shows a schematic of a solid embryo forming in contact with a perfectly flat mould wall. Assuming that the interfacial energy between phase  $\alpha$  and  $\beta$  is isotropic, it can be shown that for a given volume of phase  $\beta$  the total interfacial energy of the system is minimized if the embryo has the shape of a spherical cap with a wetting angle " $\theta$ " given by the condition that the interfacial tensions balance in the plane of the mould wall. The formation of such an embryo will be associated with an excess free energy given by:

$$\Delta G = -V_{\beta} \Delta G_{\nu} + A_{\alpha\beta} \gamma_{\alpha\beta} + A_{\beta M} \gamma_{\beta M} + A_{\beta M} \gamma_{\alpha M}$$
(12)

Where:  $V_{\beta}$  is the volume of the spherical cap;  $A_{\alpha\beta}$  and  $A_{\beta M}$  are the areas of the  $\alpha/\beta$  and the  $\beta$ /mould interfaces;  $\gamma_{\alpha\beta}$ ,  $\gamma_{\beta M}$  &  $\gamma_{\alpha M}$  are the free energies of the solid/liquid, solid/mould and mould/liquid interfaces, respectively.



Figure 5. Schematic representation of a solid embryo forming in contact with a perfectly flat mould wall.

It can be shown that for heterogeneous nucleation, Eq. [7] can be written in terms of the wetting angle and the cap radius as:

$$\Delta G_{het} = \left(-\frac{1}{3}\pi r^3 \Delta G_v + 4\pi r^2 \gamma_{\alpha\beta}\right) S(\theta) \quad (13)$$

Here,  $S(\theta)$  is the shape factor. It typically has a numerical value less than 1 depending on the shape of the nucleus.  $\Delta G_{het}$  is shown in Figure 6 along with  $\Delta G_{hom}$  for comparison. Mathematically, the relationship between the critical radii and free energy during homogeneous and heterogeneous nucleation can be shown by:

$$r_{hom}^* = r_{het}^* = \frac{2\gamma_{\alpha\beta}}{\Delta G_v} = \left(\frac{2\gamma_{\alpha\beta}T_t}{L_v}\right)\frac{1}{\Delta T}$$
 (14)

And

$$\Delta G_{het}^* = S(\theta) \Delta G_{hom}^* = \frac{16\pi \gamma_{\alpha\beta}^3}{3(\Delta G_v)^2} S(\theta) = \left(\frac{16\pi \gamma_{\alpha\beta}^3 T_m^3}{3L_v^3}\right) \frac{1}{(\Delta T)^3} S(\theta)$$
(15)



Figure 6. Schematic representation of free energy change during homogeneous & heterogeneous nucleation. Note that  $r^*$  is independent of nucleation site while  $\Delta G_{het}^*$  is lower than  $\Delta G_{hom}^*$  Overall, Eq [14] and [15] indicate that activation energy barrier against heteregogeneous nucleation  $\Delta G_{het}^*$  is smaller than  $\Delta G_{hom}^*$  by the shape factor S( $\theta$ ). Further, the critical nucleus radius, r\*, is unaffected by the mould wall and depends only on the degree of undercooling. The rate of heterogeneous nucleation may be given by the expression:

$$N_{het} = f_1 C_1 exp\left(-\frac{\Delta G_{het}^*}{kT}\right) nuclei m^{-3} s^{-1} \quad (16)$$

Where,  $f_1$  is the frequency factor similar to  $f_0$  shown in Eq [11] and  $C_1$  is the number of atoms in contact with heterogeneous nucleation sites per unit volume of liquid. It is important to realize that so far it has been assumed that the mould wall is microscopically flat. In real life, the wall is likely to contain many microscopic cracks and fissures. In such circumstances Eq. [16] will have to be modified. Heterogeneous nucleation also depends upon the microstructure of the materials system involved and dislocations/grain boundaries can often serve as nucleation sites for growth of the daughter phase.

#### 3. Growth of Secondary Phase

In a phase transition, the nucleation stage is very important and determines many features of the transformation process. However, most of the transformation product is formed during the growth stage by the transfer of atoms across the parent/ product interface. There are basically two types of interfaces: glissile and non-glissile. Glissile interfaces migrate by dislocation glide that results in shearing of the parent lattice into the product. The motion of glissile interfaces is relatively insensitive to temperature and is therefore known as athermal migration. Most interfaces are nonglissile and migrate by the more or less random jumps of individual atoms across the interface. The additional energy that the atom requires to break free from the parent phase and to attach itself to the daughter phase is supplied by thermal activation. The migration of nonglissile interfaces is therefore extremely sensitive to temperature.

Depending upon the specific physical properties of the phases involved in the phase transformation process, there are two types of atomic structures for the interface between the two phases: (1) An atomically flat close-packed interface as shown in Figure 7(a); (2) An atomically diffuse interface as shown in Figure 7(b). The major difference between the two interfaces is that in the first case, the phase transition occurs over a rather narrow transition zone where as in the second case there is a gradual weakening of the interatomic bonds and an increasing disorder across the interface. Owing to the differences in atomic structure, these two types of interfaces migrate in distinctly dissimilar ways. To illustrate an example, Figure 8 shows a schematic representation of an atomically smooth interface where the atoms are represented as cubes. In a flat interface, the minimum free energy corresponds to the minimum number of "broken bonds" on the daughter phase. Addition of a single atom onto a flat interface increases the number of broken bonds by four. Addition to a ledge increases the number of broken bonds by two and therefore a decrease in interfacial energy is noted. If the ledge contains a jog (see Figure 8) atoms from the liquid can join the solid without any increase in the number of broken bonds and the interfacial energy remains unchanged. Consequently, the probability of an atom remaining attached to the solid at jogs is much greater than that joining a facet. Smooth interfaces typically advance by the lateral growth of ledges. Since ledges and jogs are a non-equilibrium feature of the interface,

growth will be very dependent on how the jogs and ledges can be created. In a rough diffuse interface the atoms can be received at any site on the solid surface and growth at such interfaces are typically referred to a continuous growth.



Figure 7. Two categories of phase interfaces depending upon the microstructure and crystallographic properties of the two phases involved: (a) Atomically smooth; (b) Atomically rough/Diffuse interface.



Figure 8. Schematic representation of atomically smooth solid/liquid interfacewith atoms represented as cubes. Figure adapted from reference [1].

## 4. Classification of Nucleation & Growth Mechanism

A convenient way to classify nucleation and growth transformation is to divide them according to the way in which the product grows. Two major categories are identified based on whether the phase growth involves glissile and nonglissile interfaces. Transformations produced by the migration of a glissile interface are referred to as military transformations. This emphasizes the analogy between the coordinated motion of atoms crossing the interface and that of soldiers moving in a rank. In sharp contrast, the uncoordinated transfer of atoms across a nonglissile interface results in what is known as a civilian transformation.

During a military transformation, the nearest neighbors of any atom are essentially unchanged.

Therefore the parent and product phases must have the same composition and no diffusion is involved in the transformation. Martensitic transformations typically belong to this group. During civilian transformation, the parent and product may or may not have the same composition. If there is no change in composition (  $\alpha$  (bcc)  $\gamma$  (fcc) transformation in pure Fe), the new phase will be able to grow as fast as the atoms can cross the interface. Such transformation are said to be interface controlled. When the parent and product phases have different compositions, growth of the new phase is diffusion controlled. Table 1 summarizes classification of nucleation and growth mechanisms. It is important to note that this classification is taken from the work of Christiansen *et al* [3].

Туре	Military	Civilian
Effect of temperature change	Athermal	Thermally activated
Interface type	Glissile	Non-glissile
Composition of parent & product phase	Same composition	Same or different composition
Nature of diffusion process	No diffusion (mainly interface controlled)	Short-range diffusion (interface controlled); Long-range diffusion (mainly diffusion controlled)
Examples	Martensitic twining; Symmetric tilt boundary	Grain growth, precipitation; Solidification; Crystallization; Bainite condensation

#### Table 1. Classification of Nucleation & Growth Mechanisms as defined by Christian et al. [Ref 3]

#### 5. Johnson, Mehl Avrami and Kolmogorov, (JMAK) Theory: Determining Kinetic Parameters During a Phase Transformation Process

A critical issue relevant to phase transformations involves determining the volume fraction of material transformed as a function of time. For this purpose, the Johnson, Mehl, Avrami and Kolmogorov, (JMAK) theory for isothermal kinetics has been used extensively used. The application of the JMAK model to isothermal data requires that several assumptions be made about the transformation process [Ref: 5-7]:

- (1) Nucleation and growth occur at a constant temperature.
- (2) Nuclei may be used up by growing into the product phase (*ingestion*).
- (3) Nuclei may be used up by coalescence (the loss of the product interface when two or more growing nuclei merge) (*coalescence*).
- (4) A constant growth rate.

Conditions (2) and (3) are schematically illustrated in Figure 9; here, nuclei ingestion is illustrated in the top panel while nuclei coalescence is shown in the bottom panel.



Figure 9. Schematic illustration of two of the assumptions satisfying the JMAK model for

nucleation and growth kinetics. The top panel shows the ingestion of product nuclei while the bottom panel shows nuclei coalescence. Figure modified from reference [3].

The most general form of the JMAK equation is shown here:

$$\alpha(t) = 1 - e^{(-k(T)t)^n}$$
 (17)

Where,  $\alpha$  = The fraction of transformed phase (unitless); k(T) = Temperature dependent rate constant (s<sup>-1</sup>); t = Time at any point (s); n = Avrami exponent (unitless).

Here, the rate constant, k, is very sensitive to temperature while the Avrami exponent, n, is typically independent of temperature and provides information pertaining to the dimensionality of the growth mechanism. The Avrami exponent -n – is a convenient way to determine the nucleation and growth mechanism of a transforming system. The Avrami exponent can be summarized for the two distinct grown conditions (i.e. linear vs. parabolic concentration gradients) as [5,6]:

Parabolic growth: 
$$n = a' + \frac{b'}{2}$$
 (18)

And

Linear growth: 
$$n = a' + b'$$
 (19)

where: b' = growth dimensionality (unitless); a' = Represents nucleation rate (unitless); n = Experimentally determined Avrami exponent. Note that b' can take on values from 1 to 3.

Typically, b' equals 1, 2, 3 for one-, two- and threedimensionally growing particles respectively. For constant nucleation rate, a' = 1. For increasing nucleation rate, a' > 1. For decreasing nucleation rate, 0 < a' < 1. Thus, by fitting the fraction transformed, the JMAK kinetic model provides information pertaining to the nucleation rate, growth mode (linear vs. parabolic), and growth dimensionality (1, 2 or 3). For example, for site saturated nucleation (i.e. all nucleation occurs before growth begins), if growth proceeds linearly and one-dimensionally then n will be one, if growth proceeds two-dimensionally then n will be two...etc. Eq. 17 can be transformed to a linear form:

$$\ln\left(\ln\left(\frac{1}{1-\alpha}\right)\right) = n x \ln(t) + \ln(k) \quad (20)$$

Where,  $\alpha$  = The fraction of transformed phase (unitless); k = Rate constant (s<sup>-1</sup>); t = Time at any point (s); n = Avrami exponent (unitless). For a thermally activated process, the rate constant, k, is the same rate constant of the Arrhenius equation:

$$k = Ae^{-\frac{E_a}{RT}} \qquad (21)$$

Where, A = Pre-exponential factor (constant unitless),  $E_a$  = Activation energy (J/mol), R = Ideal gas constant (8.314 J/K mol), T = Temperature (K), k = Rate constant (unitless). By plotting the ln(k) vs. 1/T (the temperature at which the measurement was made) the activation energy  $E_a$  can be easily determined.

Isothermal data can be further used to obtain an estimate of the time required to complete a transformation process (i.e. the evolution times). For example, the time necessary to complete 50% of a transformation process at a constant temperature can be expressed by rearranging Eq. (17) to:

$$t = -\left[\frac{\ln(1-0.5)}{k}\right]^{1/n}$$
 (22)

Where, t = Time required for 50% completion of a phase transformation (s), k = Rate constant (s<sup>-1</sup>), n = Avrami exponent (unitless). In this way, phase metastability at intermediate temperatures of a phase transformation can be verified under isothermal measurement conditions.

It is important to note that in material science, the JMAK theory is universal if the assumed conditions in the model are not violated [8]. However, such conditions are seldom realized experimentally. Since its conceptualization in the 1960s the JMAK theory has been modified to fit experimental circumstances. Details regarding these modifications are available in the following references [9-11].

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# **RADHIKA BARUA**

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### KINETICS OF NANOPARTICLE CATALYSED BIOMASS PYROLYSIS

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#### Abstract

This study focuses on the application of  $CeO_2$  (ceria) nanoparticles as catalyst in biomass pyrolysis. Nano-sized CeO<sub>2</sub> was synthesized from its precursor, Ce(OH)CO<sub>3</sub>, which was obtained by homogeneous precipitation method. Different techniques were used to characterize the CeO<sub>2</sub> nanoparticles. The prepared nano-sized ceria particles were found to be crystalline and of nanometer dimension with a crystal size  $\sim 6.78$  nm. Catalytic activity of these nanoparticles in pyrolyzing biomass was investigated by performing pyrolysis of cellulose (major component of biomass) both in absence and presence of the ceria nano-catalyst. Effect of the catalyst on the yield, quantity and appearance of pyrolytic oils was discussed in detail. Qualitative analysis of the pyrolytic oils indicated that the synthesized CeO<sub>2</sub> nanoparticles made a positive influence on the pyrolysis phenomenon. Finally, the kinetic pathway of the biomass pyrolysis reaction in presence of the catalyst was discussed through a newly developed kinetic analysis method. The activation energy of ceria nanoparticle catalyzed cellulose pyrolysis reaction was evaluated to be 188 kJ/mol.

#### 1. Introduction

Current global energy supply is largely based on fossil fuels. Considering the depletion of fossil fuels with increase in energy consumption due to growing world population, and the issue of global warming, it is high time to opt for long-term alternative energy sources. Biomass can stand as a promising ecofriendly alternative source of renewable energy in this current energy scenario. Of late, biomass utilization in mainstream energy usage is receiving great attention as combustion of bio-fuel produces less harmful gas emissions compared to conventional fossil fuels.[1]

Biofuel can be obtained from biomass using various thermal, biological and physical processes. Among them, pyrolysis has gained more interest in producing liquid fuel product because of its advantages in storage, transport and usageversatility. Besides, pyrolysis technology has the capability to produce bio-fuel with high fuel-tofeed ratios.

The elimination of oxygen is necessary to transform bio-oil obtained after biomass pyrolysis into a liquid fuel that can be commercially accepted. Catalytic pyrolysis is a conventional method for improving the yield and quality of pyrolytic oil leading to removal of oxygen, increase in calorific value, decrease in viscosity and enhancement in stability [2]. Inorganic oxides can act as potential yet less toxic catalyst for pyrolysis to improve pyrolytic product quality. Particularly nanometer-sized oxide particles have attracted extensive interest in recent years as highly weight efficient catalysts [3]. Because, it is the external surface of particles which is used as a contact surface in catalytic processes and the specific surface area of a nanomaterial is much larger than that of a bulk material due to high surface to volume ratio. Larger the external surface area of a catalyst, higher is the contact area leading to better efficiency of catalysis.

Taking into consideration the aforementioned facts, it is thus outlined that metal oxide nanoparticles will have better catalytic activity in enhancing the performance of biomass pyrolysis. Cerium oxide (ceria) can be a promising candidate for this catalytic activity as it has already been used in various catalysis processes. This can be attributed to (a) significant oxygen storage capacity (OSC) which is largely due to the multivalent nature of cerium (shift between  $Ce^{3+}$  and  $Ce^{4+}$  states) and (b) high mobility of the oxygen vacancies at the surface of the materials. These properties, combined with the abundance of cerium on earth, make ceria a low-cost yet highly effective catalyst [4, 5]. Although ceria nanoparticles as catalysts have been studied earlier, their applicability in biomass pyrolysis has not been explored. In this work, ceria nanoparticles have been synthesized, characterized and their catalytic activity in biomass pyrolysis has been investigated. Every biomass contains cellulose as its major component which regulates the decomposition process of biomass pyrolysis. Hence, pyrolysis experiments were carried out taking cellulose as the biomass. In order to have a better insight to the mechanism of pyrolysis, it is necessary to conduct a detailed kinetic analysis of the cellulose pyrolysis process in presence of the ceria nanoparticle catalyst. For any chemical reaction, a priori knowledge of the reaction mechanism is essential to analyze its kinetics. In previously developed methods for kinetic analysis, the reaction mechanism is either assumed or identified by carrying out isothermal kinetic experiments which may not be applicable to non-isothermal reactions [6-9]. As a result, they fail to reflect the characteristics of a realistic situation. Therefore, the development of a more reliable and accurate nonisothermal kinetic analysis method is an absolute requirement. In the present study, the kinetics of cerium oxide nanoparticle catalyzed cellulose pyrolysis has been analyzed through the newly developed Deb's equation [10]. Using the equation, the actual reaction mechanism under non-isothermal conditions can be directly identified unambiguously [10]. Calculation of activation energy and determination of kinetic laws can be performed more accurately by this method. Even kinetic law(s) at any temperature that fall within the experimental range can also be established.

#### 2. Experiments and Methods

#### 2.1 Materials.

Cerium nitrate hexahydrate (Ce(NO<sub>3</sub>)<sub>3</sub>.6H<sub>2</sub>O) and urea (CO(NH<sub>2</sub>)<sub>2</sub>) of analytical grade used for synthesis of ceria nanoparticles were procured from Sigma-Aldrich and Rankem respectively. Throughout the synthesis, double distilled water was used. Cellulose used as the substrate for pyrolysis was procured from Merck.

## 2.2 Synthesis and Characterization of Ceria Nanoparticle

#### 2.2.1 Synthesis of Ceria Nanoparticle

The precursor  $Ce(OH)CO_3$  of the nanosized  $CeO_2$  was synthesized using a homogeneous precipitation method. 0.0115 mol of  $Ce(NO_3)_2.6H_2O$  and 0.0575 mol of  $CO(NH_2)_2$  were added to 60 mL of double distilled water

and stirred with a magnetic stirrer at room temperature until a homogeneous solution was obtained. Thereafter, the solution was heated upto  $115^{\circ}$ C under reflux conditions and kept at that temperature for 2 hours. During the heating, a white coloured precipitate (i.e. the precursor) was formed. Then, the precipitate was filtered and washed repeatedly. After drying at 90°C for 6 hours, this precursor was calcined in a muffle furnace at 500 °C for 1 hour to obtain the pale yellow coloured CeO<sub>2</sub> nanoparticles.

#### 2.2.2 Characterization of Ceria Nanoparticles

The crystalline structure of ceria and was identified with Rigaku Miniflex X-ray diffractometer equipped with intense Cuk<sub>a</sub> radiation ( $\lambda$ = 1.54 Å). The sample was scanned from 10° to 60° (20) with a scanning rate of 10°/min. The average crystallite size of the nanosized CeO<sub>2</sub> product was estimated by single line analysis method [11]. Morphology of the nanoparticles was studied by JEOL JSM 6390 LV scanning electron microscope. The nanoparticle size and the interplanar spacing of nanocrystals were obtained from HRTEM images taken in JEOL JEM-2100 transmission electron microscope with an accelerating voltage200 kV.

#### 2.3 Catalytic Activity of Nanosized CeO<sub>2</sub> Particles in Pyrolysis of Biomass Components

#### 2.3.1 Pyrolysis Process

The furnace of the pyrolysis setup was heated from room temperature to 400°C with a heating rate of 10°C/min. Equal amounts (5.73g) of pure cellulose and cellulose with 15% (w/w) ceria nanoparticles were placed separately inside two reactors and subjected to pyrolysis. The liquid products were collected by condensing with the help of a reflux condenser. The solid parts (char) remained inside the reactors which were collected after cooling down the setup at the end of the pyrolysis.

#### 2.3.2 Product Analysis

Gas Chromatography/Mass Spectrometry analysis of the pyrolytic oils was performed by Perkin Elmer Gas Chromatography/ Mass Spectrometry instrument with Elite-5MS capillary column. Helium was used as the carrier gas. The amount injected was 1 µl and split ratio was 50:1. The oven temperature was programmed to 120°C for 2 minutes, then allowed to rise to 270°C at a rate of 20°C/min and to stay at that temperature for 10 minutes. Total run time was 19.5 minutes. Flow rate was 1ml/min. The mass spectra obtained by GC/MS were interpreted based on an automatic library search (NIST).

#### 2.3.3 Kinetic Analysis of the Catalysed Pyrolysis Process

Differential Scanning Calorimetry experiments presented in this paper were performed by using a Perkin Elmer DSC instrument. DSC curves were obtained with selected heating rates 8°C/min and10°C/min from room temperature to 600°C. By measuring the relative areas covered by each DSC plot at different temperatures while progressing from initial temperature to final temperature, fractional conversion values at those temperatures were calculated. Using these values, order of the reaction was identified and activation energy was calculated from Deb's equation [10].

#### 3. Results and Discussions

#### 3.1 X-ray Diffraction Analysis of Ceria (CeO<sub>2</sub>) Nanoparticles

XRD pattern of the synthesized nanoparticle (**Figure 1**) showed peaks at  $28.52^{\circ}$ ,  $33.00^{\circ}$ ,  $47.48^{\circ}$ ,  $56.33^{\circ}$ , which were due to (111), (200), (220), (311) lattice planes respectively. This was in well agreement with the standard JCPDS file for the XRD pattern of pure CeO<sub>2</sub> with FCC crystal structure (JCPDS 81-0792). Prominently broad diffraction peaks distinctly indicated that the products were of nanometer dimension. The crystallite size was calculated to be 6.78 nm and the lattice strain was 0.010893.



Figure 1. XRD pattern of CeO<sub>2</sub> nanoparticles

#### 3.2 SEM Analysis of Ceria(CeO<sub>2</sub>) Nanoparticle

SEM image of the nanoparticles (**Figure 2**) showed mostly agglomerated structures of irregular shapes. This agglomeration is attributed to the tendency of ceria to absorb moisture.



Figure 2. SEM image of CeO<sub>2</sub> nanoparticle

#### 3.3 TEM Analysis of Ceria (CeO<sub>2</sub>) Nanoparticles

TEM micrograph of the ceria samples revealed agglomerated structures of nanosized cerium oxide particles (**Figure 3a**). From SAED pattern (**Figure 3b**), poly-crystalline nature of the  $CeO_2$  nanoparticles was confirmed and (111), (200), (220) lattice planes of the crystal structure were identified.



Figure 3a. TEM micrograph of CeO<sub>2</sub> nanoparticlesb SAED pattern of CeO<sub>2</sub> nanoparticles

#### 3.4 Evaluation of Catalytic Activity of Nanosized Ceria Particles

Characteristics of the bio-oils obtained from cellulose pyrolysis with and without catalyst were studied both quantitatively and qualitatively. Pyrolytic oil from the pure cellulose pyrolysis was a double phase (oil+ aqueous layer) liquid (**Figure 4a**), whereas the ceria nanoparticle catalysed pyrolysis gave a single phase liquid with a comparatively darker appearance (**Figure 4b**).



Figure 4a. Pyrolytic liquid obtained from pure cellulose pyrolysis b Pyrolytic liquid obtained from CeO<sub>2</sub> nanoparticle catalyzed cellulose pyrolysis. The yield of bio-oil from pyrolysis of 5g of pure cellulose (after separating out the aqueous part) increased from 1 mL to 1.1 mL when the pyrolysis was conducted adding 15%(w/w) ceria nanoparticles to cellulose. Hence, a substantial increase (10%) in the yield of pyrolytic oil was observed due to addition of nanosized cerium oxide particles which is a significant improvement. This proves that use of cerium oxide nanoparticles as a catalyst considerably enhanced the pyrolysis phenomenon.

A large number of polar organic compounds were detected in the pyrolyticproducts through GC/MS analysis. The major products obtained from pyrolysis of cellulose in absence and presence of ceria nanoparticles as catalyst are shown in **Table 1**. Pyrolytic products of cellulose contained levoglucosan and furan ring derivatives as the predominant products. After addition of catalyst, a number of lower molecular weight compounds were obtained along with these compounds. This indicates that  $CeO_2$  nanoparticles indulged in C-C bond scission reactions during cellulose pyrolysis.

#### Table 1. Constituents of Pyrolytic Oils of Cellulose

From Pure Cellulose	From Cellulose with CeO2 Nanoparticles
5-Methyl-2-furancarboxaldehyde	2- Hydroxymethylcyclopentanol (cis)
3,4-Furandimethanol	1,4:3,6-Dianhydro- α-D-glucopyranose
1,4:3,6-Dianhydro- α-D-glucopyranose	2- (1,1- Dimethylethyl)-cyclobutanone
D- allose	4- Hexen-3-one
1,6-Anhydro- $\beta$ -D-glucopyranose (Levoglucosan)	1,6-Anhydro- $\beta$ - D- glucopyranose (Levoglucosan)

#### 3.5 Kinetic Analysis of Cellulose Pyrolysis Catalysed by Ceria Nanoparticles

The DSC plots for the sample (cellulose + 15% CeO<sub>2</sub> nanoparticles) at two different heating rates (8°C/min and 10°C/min) exhibited almost similar thermal characteristics (**Figure 5 a and b**).



# Figure 5. DSC plots of cellulose with 15% CeO<sub>2</sub> nanoparticles at heating rates a 8°C/min and b 10°C/min

Fractional conversion ( $\alpha$ ) values were evaluated from each of these DSC plots by measuring relative areas under the pea kat different temperatures while proceeding from initial temperature to final temperature (**Figure 6 a and b**).



# Figure 6. Plots of fractional conversion of the reactant with temperature at heating rates a 8°C/min and b 10°C/min

According to a new method of kinetic analysis developed by Deb [10], kinetic equation for any reaction progressing under non-isothermal condition at a heating rate  $\beta_i$  has been proposed as

$$\ln[g(\alpha)/T_{f}^{2}] = \ln[A(T_{f}-T_{i})/T_{f}^{2} - A(T_{f}-T_{i})/T_{f}^{2} \ln \{1-E/RT_{f}\}] - E/RT_{f}[1+RT_{f}/E \ln\beta_{i}]$$
(1)

where  $g(\alpha)$  is the reaction mechanism which is expressed as an appropiate function of fractional conversion  $\alpha$ ;  $T_i$  and  $T_f$  are the initial and final temperatures respectively. E and A are the kinetics parameters representing the activation energy and the pre-exponential factor while R is the universal gas constant.

The logarithmic term of the right hand side of (1) remains almost constant. In that case, for any  $g(\alpha)$  value corresponding to a temperature T, this equation can be generalized as

$$\ln[g(\alpha)/T^{2}] = -E/RT[1+RT/E \ln\beta_{i}] + Const$$
(2)

Therefore, a plot of  $\ln[g(\alpha)/T^2]$  versus 1/T for different T and respective  $\alpha$ -values should yield a straight line with slope E/R[1+RT/E  $\ln\beta_i$ ] from which activation energy of the reaction can be calculated.

Deb's kinetic method revealed that the rate law which remained operative during the ceria nanoparticles catalyzed cellulose pyrolysis resembled to a **'one and a half order'** reaction. The experimentally obtained  $g(\alpha)$  value for such a reaction is  $\{(1-\alpha)^{-1/2}-1\}$ . Putting this value of  $g(\alpha)$  in (2), kinetic equation of this particular reaction is attained as

$$\ln[\{(1-\alpha)^{-1/2}-1\}/T^2] = -E/RT[1+RT/E\ln\beta_i] + Const$$
(3)

Plotting  $\ln[\{(1-\alpha)^{-1/2}-1\}/T^2]$  against 1/T for a number of  $\alpha$  values corresponding to different T values, a straight line was obtained (**Figure 7**).



## Figure 7. Activation energy estimation from ln $[{(1-\alpha)^{-1/2}-1}/T^2]$ vs 1/T plot

From the slope of this straight line, activation energy for nanosized  $CeO_2$  catalyzed pyrolysis of cellulose was calculated to be 188.19KJ/mol.

#### 4. Conclusion

To enhance the performance of cellulose pyrolysis,  $CeO_2$  nanoparticles were synthesized and used as catalyst in pyrolyzing cellulose. The evaluation of catalytic activity of the developed  $CeO_2$  nanoparticles in pyrolyzing cellulose was carried out on the basis of qualitative and quantitative studies of the pyrolytic oil. The results indicated that the ceria nanoparticles could improve the pyrolysis process significantly. A kinetic analysis method proposed by Deb to study non-isothermal reactions was used to analyze the kinetics of the catalyzed biomass pyrolysis with the help of DSC experiments. The analysis resulted in successful determination of the order of the reaction and consequent estimation of the activation energy.

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Brief Biography: Pritam Deb is currently an Associate Professor in Department of Physics at Tezpur University (Central University), Tezpur, India. He obtained his Ph.D. on nanoscience from Jadavpur University in 2003. After a string of brief scientific visits in prominent research laboratories in Europe, he joined Tezpur University, India in 2004. In recent times, he held positions of Max Planck fellow of Max-Planck-Institut für Eisenforschung, Germany; Golden Jubilee Fellow of Banaras Hindu University; Associate of S.N. Bose National Research Centre for Basic Sciences, Kolkata. His research interest spans over fundamental areas like quantum confinement effect, magnetism in low dimension etc to interdisciplinary areas like biomedical nanotechnology, molecular imaging etc. His overall research contributions exemplify innovativeness and originality in applications of fundamental principles of physics to solve critical issues in low dimensional structures. One of the important research contributions by him is in the area of kinetic studies of heterogeneous solid state processes. He proposed a new, more realistic and accurate nonisothermal kinetic analysis theory and procedure without any a priori knowledge of the mechanism. This method derives actual reaction mechanism and hence a more accurate activation energy of the process. Applicability of the method in several systems has also been revealed. He has developed software based on this kinetic analysis method to determine the mechanism and activation energy. The research achievements of him in this brief stint have been credited by two patents, two software copyrights and fifty publications. He has also authored two books. As a teacher, Deb was instrumental in developing masters' course on nanoscience and technology in his university in 2005 and also several new subject courses in masters and pre-Ph.D. level. His achievements as an academician, researcher and visionary are all directed towards meeting the ultimate societal objectives of balanced growth in all spheres with the help of the powerful tool of education and research. So far, his academic accomplishments have been acknowledged by way of peer recognition through several national and international awards. He has received many coveted awards namely – Young Scientist Research Award, DAE, Govt of India (2007); Young Scientist Award, ISCA (2003); Young Scientist Award, MRSI (2001); DST award for representing India in Lindau Nobel Laureates Meeting (2005); MMD Gold Medal Award, Institution of Engineers (2005); BHUMET Golden Jubilee Fellowship (2003-04) and Max Planck Fellowship of Max Planck Society, Germany (2009-12).

### FIRST ORDER MAGNETO-STRUCTURAL PHASE TRANSITION AND ITS IMPLICATIONS ON THE FUNCTIONAL PROPERTIES OF Fe-Rh BASED ALLOY SYSTEM.

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#### 1. Introduction

First order phase transitions are quite commonly experienced in our daily lives during phenomena like boiling of water to vapor or solidification of water to ice. These phase transitions have an associated latent heat of transformation [1]. Metastability and phase coexistence of the two competing phases involved in the transition are the other generic features of such first order transitions, irrespective of the underlying microscopic interaction or the nature of phases involved in the transition. It is more common to see the coexistence of water and ice over a broad temperature regime instead of a sudden transformation of the entire volume of water to ice. Such single shot transformations take place only in ultra-pure single element systems like Dy single crystal [2]. If we consider the water-ice system, it is observed experimentally that very pure water can be cooled below  $0^{\circ}$ C (the thermodynamic transition temperature of water-ice system) without the formation of ice at normal atmospheric pressure. The liquid phase (water) is then said to be metastable as it has a higher free energy compared to that of ice at the same temperature. Cooling below the thermodynamic transition temperature while still retaining the high temperature phase is termed as supercooling [3]. Similarly the low temperature phase can be *superheated* above the thermodynamic transition temperature before the transformation occurs. Thus the metastability across the phase

transition leads to a hysteresis of the observed physical property as a function of the thermodynamic variable like temperature or pressure which drives the transition [3]. The observation of hysteresis can be a useful tool if the latent heat is difficult to measure across a first order phase transition [4]. The difficulty in measuring latent heat usually arises from the broadening of the phase transition due to underlying static quenched-in disorder in form of impurities, defects and dislocations in the system [5]. These impurities act as nucleation sites of the product phase in the parent matrix, e.g. small particles of dirt inside water act as locations where the first nuclei of ice are formed. The distribution of the impurities thus influences the nucleation and growth dynamics which leads to interesting phenomenon as we see later during the course of this article. The influence of disorder on the kinetics of a first order transition can be so vital in certain cases that the survival of certain species solely depends on whether or not their body fluids freeze during the harsh winter conditions in the arctic region. The painted turtle, for example, is known to keep its surface and internal organs so clean that it can prevent the solidification of body fluids down till temperatures as low as -15° C [6]. The survival of trees and certain fish near the North Pole without freezing are also some examples of tuning the nucleation and growth kinetics by controlling the levels of disorder.

First order transitions can also occur in form of a transformation from one lattice (or spin) structure to another inside a solid as a function of temperature, pressure and magnetic field [3,4]. The same generic features of metastability and phase coexistence are observed across such transitions. While the nucleation and growth dynamics across a liquidsolid transition can influence the survival of certain species in nature, the same nucleation and growth dynamics across first order transitions in solids can be controlled in a laboratory to achieve a desired functional response of materials which can be of technological importance [7]. In this article, we explore the characteristic features of a first order magneto-structural transition in a Fe-Rh based alloy system which is known to show interesting functional properties of potential technological applications near room temperature.

The Fe-Rh alloy system has attracted considerable interest due to giant magnetocaloric effect (MCE, change in temperature due to adiabatic application of magnetic field) [8], giant elastocaloric effect (change in temperature caused by application of mechanical stress) [9], giant magnetostriction (change in volume by the application of external magnetic field) [10] and giant magnetoresistance (GMR, change in electrical resistance by the application of external magnetic field) [11] occurring close to room temperature. We believe that such wide range of functionality of this alloy system arises due to a first order transition from an antiferromagnetic (AFM) to ferromagnetic (FM) state driven by both temperature (T) [12] and magnetic field (H) [13]. This magnetic transition is also accompanied by a structural distortion [13]. It was believed for quite some time that though Fe-Rh exhibits a giant MCE close to room temperature, the MCE vanishes after the first field cycle [14, 15].

In this article we present the results of our work which has solved this long-standing problem. We show that the possible role of phase coexistence and associated metastability across the first order magneto-structural transition in tuning the functional properties of this material has largely gone unnoticed. Such phase coexistence and metastability across the first order magnetostructural transition in Fe-Rh alloys give rise to interesting thermomagnetic history effects in the observed physical properties like magnetization and magnetostriction. We clearly show that the vanishing of the giant magnetocaloric effect in Fe-Rh was a misinterpretation of the thermomagnetic history effects, which are expected to occur across any first order transition driven by two variables like temperature and magnetic field. Apart from establishing the general nature of the thermomagnetic history effects, we also attempt to find the similarity between the nucleation and growth dynamics across a first order transition with the crystallization process of solids formed out of melts. This understanding is then used to model the response of a material exposed to multiple cycles of temperature inside the hysteretic region across a first order transition. We also show that under certain circumstances, the kinetics of the first order transition can get arrested and a glass-like state can arise which is now termed as the "magnetic glass". This article highlights that, apart from having a large value of the functional property (e.g. magnetocaloric effect or magnetostriction), it is also necessary to understand the nucleation and growth mechanism (which is governed by the underlying disorder) across a first order phase transition, if such materials are to be used for reproducible technological applications under multiple temperature or magnetic field cycles.

#### 2. Experimental Methods

The polycrsytalline parent Fe-Rh and Ni doped Fe-Rh alloys were prepared by arc melting the constituent elements in an argon atmosphere. Details of heat treatment and characterization can be found in ref. [16]. Temperature dependent ac susceptibility was measured using a home-made apparatus. Magnetization (*M*) measurements were performed using a commercial SQUID magnetometer (Quantum Design, MPMS-5) and Vibrating Sample Magnetometer (VSM, Quantum Design). Magnetic force microscopy (MFM) imaging was performed using a commercial instrument (NT-MDT, SOLVER-PRO). The linear thermal expansion was measured using a home-made set-up based on the strain gauge technique [17].

#### 3. Phase Coexistence: Bulk Measurements

Phase coexistence across a FOMST has been widely studied in the case of manganites showing colossal magneto-resistance (CMR) [18, 19]. Such phase coexistence is now observed in various other classes of magnetic materials like CeFe<sub>2</sub> based pseudobinaries [20] and giant magnetocaloric material namely  $Gd_5Ge_4$ [21], suggesting the generality of this phenomenon. Such multi-scale phase coexistence which is observed even up to the micrometer scale can be explained by a coupling between the electronic and elastic degrees of freedom [22]. Here we first study the signatures of phase coexistence through bulk ac susceptibility measurements and then provide an explicit experimental evidence of the intricate relationship between structural and magnetic transition on the sub-micron scale in Fe-Rh using MFM. Our results provide support to the proposed theoretical framework [22], and further emphasize that phase coexistence and metastability are generic features

associated with any system undergoing a FOMST and are not limited to only CMR manganites.



#### Fig. 1. Temperature dependent ac susceptibility in a magnetic field of $3.4 \times 10^{-4}$ T rms while heating and cooling the sample. See ref. [16].

Fig. 1 shows ac susceptibility as a function of Tacross the AFM to FM transition both while heating and cooling the sample. The transition shows a thermal hysteresis of about 10K. The hysteresis curve which encloses both the reversible regions at the low-*T* and high-*T* end is known as the envelope curve. Phase coexistence across this transition can be verified by using the technique of minor hysteresis loops (MHL) [23]. A minor hysteresis loop is generated by reversing the direction of temperature change inside the hysteretic region on the envelope curve before reaching the reversible region. The minor loops showing hysteresis is an indication of the coexistence of the competing phases at the temperature of initiation of the loop. If there is no coexistence of the two phases, then the minor loops won't show any hysteresis. The other aspect to be noticed about the envelope curve is that the onset of the AFM to FM transition during heating is nearly 300K while that of the FM to AFM transition while cooling is about 350K. A situation

where the onset temperature while cooling is larger than that while heating, can arise mostly when the transition is influenced by disorder [24]. It is known that random quenched-in disorder can smear out a first order transition to an extent of complete rounding off of the transition [5]. Furthermore, strain produced in the sample matrix during a structural transition can couple these isolated defects and lead to the formation of a landscape of free-energy minima [22].

#### 4. Phase Coexistence: Local Measurements

The applicability of the landscape model can be verified by imaging the transition process using a local probe. Fig. 2 shows the imaging of the time evolution of the AFM to FM transition using MFM. AC technique was used for MFM imaging where the cantilever is oscillated at or near its resonance frequency. The magnetic interaction acts through a force gradient on the tip to produce a shift in the resonant frequency. This shift in the resonance frequency is detected in terms of shift in the phase of cantilever oscillation [25]. A non-zero phase shift indicates the presence of a FM cluster. The map of the phase shift over the scan area constructs the MFM image. The magnetic information is separated from the topographic information by performing the measurement in two different passes over the same region of the sample. The first pass provides the topography of the sample. This information is then used as a reference surface for the second pass with the tip lifted by about 30 nm. Thus the second pass measures forces originating mostly from magnetic interaction, which fall off much more slowly compared to the van der Waals forces [25]. For the measurements shown in fig. 2, the sample was dipped directly in liquid nitrogen (LN<sub>2</sub>) and then brought back to room temperature. With this

temperature history, the sample is now mostly in the AFM state very close to the onset of the FM state as seen from figure 1. This is also quite evident from the MFM image  $(M_0)$  of fig. 2 where the FM state is yet to develop. To study the time evolution (dynamics) of the AFM to FM transition, we now focus our attention on the place marked as 'A' on the 3D topography and the MFM image of fig. 2. At time t=0, the place marked 'A' on the topography  $(T_0)$  has a height of about 40 nm and is the largest defect site on the surface. This defect site acts as a nucleation centre for the first nucleus of the FM phase. The images (T1) and (M1) in fig. 2 were obtained after 1 hour. As can be seen, the magnetic signal (FM state) at location 'A' has increased to slightly more than 4° from a fraction of a degree in figure 2 (M0). The AFM to FM transition is also coupled to a structural distortion in which the volume of the unit cell in the FM phase is slightly larger [13]. Correspondingly, the height of the location A has also increased to slightly more than 50 nm (see fig. 2 (T1)). After another 1 hour (t = 2 h), new blisters appear on the topography (T2) and the MFM (M2) image. These regions are marked as 1, 2 and 3. At t = 2h, the height of the location 'A' has also increased to almost 70 nm with a corresponding increase in the magnetic signal at the same location. Eventually after 3 hours, almost the entire sample surface gets crowded with these nuclei of the product FM phase ((T3) and (M3)). This observation shows that not only the growth of the individual nucleus but also the formation of newer nuclei is governed by the intricate coupling between the surface topography and the magnetic structure. These results show that a framework, which takes into account only static and isolated quenched-in disorder [5] to explain phase coexistence across the transition, could be quite insufficient. The formation of newer nuclei can be explained when a mechanism is present where the

static impurities are correlated through a long-range field. In case where a system undergoes structural transition, cooperative lattice distortions and the associated modification in the strain fields provide a natural way to couple the isolated pockets of disorder already present [26]. The lattice distortion (change in topography) is accompanied with a coexistence of the two magnetic phases (fig. 2 (M2)). This observation follows the theoretical model by Ahn et al., [22] where the structural aspect is necessary to explain phase coexistence at micrometer scales.



Fig. 2. Time evolution of topography (T0, T1, T2 and T3) and the corresponding magnetic information (M0, M1, M2 and M3) obtained from Magnetic Force Microscopy measurements. Reproduced from ref. [27]

#### 5. Nucleation and Growth Dynamics

Having established the phase coexistence through bulk and local measurements, we now try to find the common features between a general first order transition driven by temperature and magnetic field and the time dependent crystallization of solids from sufficiently undercooled melts. Crystallization process or the nucleation and growth dynamics, in general, during transformations in solids has been a subject of great interest [28, 29]. The solidification and melting transitions are known to be of a first order nature and attempts have been carried out to establish the common features in such transitions with first order transitions in other systems. It has been shown that the vortex lattice in a type-II superconductor melts like ice melting to water [30]. To understand the common features of solidification process and other first order transitions, it is first necessary to measure the phase fraction of the competing phases and study its evolution with respect to the external thermodynamic variable like temperature or magnetic field. It is relatively straightforward to estimate the phase fraction using local imaging of the phase transition process [31], but quite difficult by using bulk measurements. The reason is that in a bulk measurement across a magnetic transition, the measured property like susceptibility or magnetization is a vector sum of all the individual values. We have studied the bulk magnetization and ac susceptibility across the first order AFM to FM transition in Fe<sub>0.975</sub>Ni<sub>0.025</sub>Rh to establish the similarity of a general first order transition with that of a crystallization process [32]. The magnetic relaxation measurements across the temperature and field driven transition show a power-law dependence with a non-monotonic behaviour of the exponent as a function of temperature and magnetic field. This non-monotonic behaviour of the exponent of this power law hints towards a nucleation and growth mechanism which is similar to the solidification process from melt [32]. The nucleation and growth mechanism of crystallization of solids from melt as a function of time is described phenomenologically by the Avrami model [33]. The central assumptions of the Avrami model are as follows:

- The new phase is nucleated by germ nuclei which already exist in the parent matrix.
- The density of these germ nuclei diminishes through activation of some of these into growth nuclei and the coalescence of these nuclei in to the product phase.
- The growth rate is independent of the transformed phase and only depends on the untransformed phase
- The nucleation events are considered to be random and the nuclei are allowed to freely overlap with each other during the growth process.

This model gives the evolution of phase fraction as a function of time in terms of an equation:

$$f = 1 - \exp(-kt^{\eta}) \tag{1}$$

and is known as the Kolmogorov-Johnson-Mehl-Avrami (KJMA) relation. Here 'k' is related to the activation energy and ' $\eta$ ' is the Avrami exponent,



Fig. 3. Temperature dependence of the areas of MHLs inferred from the ac susceptibility measurements on  $Fe_{0.975} Ni_{0.025} Rh$ . The areas of MHLs are related to the phase fraction of the ferromagnetic phase. Reproduced from ref. [32]

which is related to geometrical factors. This equation gives the famous 'S' shaped curve when the phase fraction is plotted as a function of time. As mentioned earlier, the relaxation measurements of bulk magnetization show a time dependence which is a power law and not the same as predicted by the KJMA relation. We have therefore proposed that the area of MHLs can be treated as the measure of phase fraction during the phase transition process. The generalization of the Avrami law from 'time' to 'temperature' or 'field' can then be carried out by studying the evolution of phase fraction across the corresponding phase transitions.

Fig. 3 shows the normalized area of MHLs with respect to the area under the envelope curve (or the phase fraction). The curve resembles the 'S' shaped curve and can be fitted by the relation:

$$f = 1 - \exp(-k(T - T_0)^{\eta})$$
 (2)

Here  $T_0$  is the onset temperature of the transition. The same relation holds true even for field induced transition with 'T' replaced by 'H'. Fig. 4 shows the evolution of phase fraction as a function of magnetic field and the fit of the experimental data with the KJMA curve. The phase fraction across the field-induced transition can be fitted with

$$f = 1 - \exp(-k(H - H_0)^{\eta})$$
 (3)

where  $H_0$  is the onset field of transition. These



Fig. 4. Magnetic field dependence of the areas of MHLs during magnetization measurements on Fe<sub>0.975</sub>Ni<sub>0.025</sub>Rh. Reproduced from ref. [32]

results show that the area of MHLs can be indeed treated as a measure of the phase fraction of the competing phases across the phase transition. The heuristic argument for taking the area of MHL as the phase fraction is as follows. The envelope curve is the hysteresis curve which encloses both the reversible low-temperature and high-temperature phases. During the heating cycle of the envelope curve, the entire sample transforms from the antiferromagnetic to ferromagnetic phase. Similarly, the cooling curve represents the entire sample transforming from the ferromagnetic to antiferromagnetic phase. If a minor loop is initiated at any intermediate temperature value, it exhibits a smaller hysteresis compared to the hysteresis obtained on the complete envelope curve. A minor loop shows hysteresis when both the phases involved in the transition coexist. The MHL initiated at a lower temperature encloses a smaller area compared to MHL initiated at a higher temperature as the amount of the ferromagnetic phase at lower temperatures is lower during the heating cycle. Thus growing ferromagnetic fraction is also accompanied with the growing area of MHL. If we (hypothetically) divide the entire sample into smaller volumes, each hysteresis loop (envelope curve or MHL) can be thought of as a superimposition of smaller hysteresis loops for each of these volumes. Thus the area of a hysteresis loop initiated at any temperature, which is an addition of smaller hysteresis loops, would represent the volume of the transformed phase at that temperature. If we take the area of envelope curve as unity, the normalized area of each MHL can then be taken as the phase fraction of the product phase at the temperature of initiation of MHL.

#### 6. Modeling of Minor Hysteresis Loops

The assumption of different locations of the sample having their own independent hysteresis was explored further by measuring thermal expansion across the transition in  $Fe_{0.955}Ni_{0.045}Rh$  [34]

Figure 5 shows some of the representative MHLs in strain measurements which are initiated during the heating cycle across the first order transition in  $Fe_{0.955}Ni_{0.045}Rh$ . The presence of hysteresis and phase coexistence (resulting in MHLs) across the transition means that the value of the measured physical property not only depends on the value of the driving force (temperature, in this case) but also on the history of reaching to a particular value

of the control parameter. The output is then a multivalued function of the input. This fact is of significant importance if the physical property (presently, strain) is to be used for technological applications where the device undergoes numerous cycling of the driving force. Specifically, if the material is cycled to and fro inside the hysteretic regime, it becomes necessary to be able to predict the entire path of evolution of the output if a successful device is to be constructed. Such a situation may arise if the entire available range of the strain across the transition (0.4% in our case) is not required for the desired application.



Fig. 5. Strain v/s Temperature during heating and cooling in  $Fe_{0.955}Ni_{0.045}Rh$  and representative minor hysteresis loops on the heating cycle.



Fig. 6. The definition of an elementary hysteresis operator according to the Preisach model.

The MHLs inside the hysteretic region were modeled using the Preisach model of hysteresis which was originally proposed for explaining the hysteresis of ferromagnets [35]. The basic assumption of the Preisach model is that the complete hysteresis curve can be thought of as a summation of elementary hysteresis operators (or hysterons) defined in fig. 6.

This assumption is similar to the assumption used for identifying the phase fraction discussed earlier. The switching operator is chosen such that  $\gamma_{\alpha\beta} \times T$  is either 0 or 1, where T is the input. The value of the hysteresis operator switches to 1 at T =  $\alpha$  on the temperature increasing cycle and switches back to 0 at T =  $\beta$  during the temperature decreasing cycle. The output  $\varepsilon$ (T) is then given by,

$$\varepsilon(T) = \iint_{\alpha \ge \beta} \mu(\alpha, \beta) [\gamma_{\alpha\beta} T] d\alpha \, d\beta \tag{4}$$

where  $\mu(\alpha,\beta)$  is the weight factor associated with each hysteresis operator. By using this relation, the behaviour of MHLs can be modeled for multiple temperature cycles. More details of this calculation can be found in ref. [34] which uses the experimental data at close temperature steps.



Fig. 7. The experimental data (open circles) along with the calculated curves using the Preisach model as described equation 4.

Fig. 7 shows one such case of two MHLs generated for multiple temperature cycles. The bigger MHL is generated by decreasing the temperature from  $\alpha_1$  to  $\beta_1$ , subsequently increasing the temperature to  $\alpha_2$  and then finally reducing the temperature to below  $\beta_1$ . The MHL is generated by following the path  $\alpha_1$ - $\beta_1$ - $\alpha_2$ - $\beta_2$ - $\alpha_3$  and then reducing the temperature to  $\beta_3$ . The solid lines are the calculated curves using equation 4 which describe the experimental results quite well. However, the Preisach model fails beyond a certain temperature or at the 'tails' of the transition, where there is a crossover from nucleation dominated process to growth oriented process. The growth and coalescence of nuclei may contradict the basic assumption of independent hysteresis loops. Probably after a particular length scale of coalescence, the different pockets of the transformed phase may influence each other and no longer remain independent. More details can be found in ref. [34]

#### 7. Thermomagnetic History Effects

So far we have discussed the history effects arising due to the nucleation and growth process across a first order transition driven by only a single variable like temperature. Interesting history effects also arise when the transition is driven by two thermodynamic variables like temperature and magnetic field. We show that the study of such phase coexistence and related history effects is important because they influence the functional properties of Fe-Rh like the giant MCE near room temperature [36]. We also show how the understanding of these history effects can be used to achieve reproducible response from a material which undergoes a first order transition.



Fig. 8. Isothermal magnetization as a function of field at (*a*) 290K and (*b*) 305 K. See ref. [16].

Figure 8 shows isothermal *M*–*H* curves across the field induced transition in the parent Fe-Rh alloy at two representative temperatures, which are 290K and 305K. For both these measurements, the sample was warmed up to the desired temperature in zero field from temperatures well below 200 K, where the sample is completely in the AFM state [16]. A sudden increase in magnetization during the first field increase (virgin curve) is a signature of a field induced (metamagnetic) transition. The transition shows a hysteretic behaviour on decreasing the field. The nature of the hysteresis across the transition is quite different compared to the M-H hysteresis observed in case of ferromagnets. On the second

H-increasing cycle (envelope curve) we see that the virgin curve lies outside the envelope curve. During subsequent isothermal H cycles, the envelope curve is retraced irrespective of the number of cycles and the virgin curve is lost for that isothermal M-H cycle.



Fig. 9. H – T phase diagram of Fe<sub>48</sub>Rh<sub>52</sub>

The phenomenon of the virgin curve lying outside the envelope curve can be explained by using the *H*–*T* phase diagram for our Fe–Rh alloy, which is shown in fig. 9. This H-T phase diagram has been determined through a detailed study of ac susceptibility and magnetization [16]. The  $(H^*, T^*)$ line marks the limit of supercooling of the FM phase. Between the  $(H^*, T^*)$  line and the  $(H, T)_{onset}$  (AFM to FM) line, the supercooled FM phase (SC FM) can coexist with stable AFM phase during the T and/or Hdecreasing cycle. Beyond the  $(H^{**}, T^{**})$  line, the sample is in the stable FM phase. In the region between the  $(H, T)_{onset}$  (AFM to FM) and  $(H^{**}, T^{**})$ lines, the sample is in the phase coexistent state where the partly converted FM phase coexists with the metastable AFM phase. The fraction of the AFM phase decreases as the  $(H^{**}, T^{**})$  line is approached by either increasing T or H [16]. For the isothermal H-increasing cycle at 290K shown in fig. 8(a) (the

path marked as 2 in fig. 9), the starting point of the isothermal H cycle is single phase stable AFM. The sample partly gets converted to FM phase during the isothermal increase in H. This FM phase can be supercooled when H is isothermally reduced back to zero and then leads to a higher value of M on the subsequent H-increasing cycles. For the isothermal *H*-increasing cycle at 305K shown in fig. 8(b) (the path marked as 3 in fig. 9), the starting condition of the sample is that of a small fraction of partly converted FM phase coexisting with a large fraction of the AFM phase. Most of this AFM phase gets converted to stable FM phase during the isothermal increase in *H*. This FM phase persists even when *H* is isothermally reduced back to zero [16] and is then carried over during the next isothermal H-increasing cycle giving rise to higher value of M on the envelope curve. This observation shows that if the working temperature of Fe-Rh is to be confined between 280 and 360 K, which could be of interest for magnetic refrigeration near room temperature, the virgin curve will always be outside the envelope curve. This loss of virgin curve was thought to be the cause behind the vanishing of MCE after the first field cycle [8, 14, 15].

## 8. Influence of History Effects on Functional Property

With this background, we proceed to estimate the change in magnetic entropy (magnetocaloric effect) for an isothermal cycle. The magnetic entropy is calculated by using the integral Maxwell relation approximated for M-H curves measured at discrete T intervals [37] and is given by,

$$\Delta S_m \approx \frac{1}{\Delta T} \Big[ \int_0^H M(T + \Delta T, H) dH - \int_0^H M(T, H) dH \Big]$$
 (5)

Thus the area under the isothermal M-H curve from 0 to upper limit H (5 T in our case) at a particular temperature T can be subtracted from the area under the M-H curve at a higher temperature  $T + \Delta T$  to estimate the change in magnetic entropy at the temperature  $(T + \Delta T/2)$ . Each isothermal measurement during the H-increasing cycle gives the virgin curve and the envelope curve. This gives four combinations for calculating the  $\Delta S_{m}$ . These are:

- (1) area under the virgin M-H curve at T to be subtracted from area under the virgin M-Hcurve at T+ $\Delta T$ ,
- (2) area under the virgin M-H curve at T to be subtracted from area under the envelope M-Hcurve at T+ $\Delta T$ ,
- (3) area under the envelope M-H curve at T to be subtracted from area under the virgin M-Hcurve at T+ $\Delta T$ , and
- (4) area under the envelope M-H curve at T to be subtracted from area under the envelope M-Hcurve at T+ $\Delta T$ .

The MCE in Fe–Rh is inverse, i.e. the sample cools by adiabatic increase in H [8]. If the adiabatic Hincreasing cycle is started at the zero-field point of path 3 in fig. 9, the sample reaches at the  $\mu_0 H = 5$  T point at a lower T (say path 2). When H is reduced isothermally along path 2, some amount of FM phase will remain supercooled as discussed earlier. This means that even if the adiabatic cycle is started in the virgin state at a higher temperature, the low temperature state corresponds to the envelope curve. Thus the second mathematical possibility of subtracting the area under the virgin M–H curve at Tfrom the area under the envelope curve at  $T + \Delta T$ cannot be achieved physically and has to be ruled
out. Also, the first possibility from the above list would be difficult to achieve physically but we still retain it for the sake of comparison.



## Fig. 10. MCE as a function of temperature for three possible histories of the sample.

Figure 10 shows the  $\Delta S_m$  as a function of T for the three possible histories listed above [38]. The variation in MCE clearly shows the history dependence. It can be clearly seen that when the difference between the areas of the virgin curve at a higher temperature and the envelope curve at a lower temperature is taken, the MCE reduces drastically compared with the differences in areas of the virgin curves at the same temperatures. This is what was noted by Annaorazov et al [8] and has later been accepted generally. We, however, see that if the difference in areas between two envelope curves is taken, the MCE actually increases marginally compared with the virgin cycle. Thus for a refrigeration cycle using Fe-Rh, the first H-increasing and decreasing cycle at higher temperature needs to be isothermal. The adiabatic *H*-increasing cycle can then be carried out during the second field increase to achieve a high entropy change. If the envelope curve is used for magnetic

cooling, the effective refrigerant capacity  $R_{\rm eff}$  (i.e. refrigerant capacity after subtracting the hysteresis loss) turns out to be 324.42 J kg<sup>-1</sup> with the hot end at 311.8 K and cold end at 268.6K of the refrigerator. This is one of the largest known values near room temperature.

We have used this method of achieving a reproducible MCE across the first order AFM to FM transition in  $Fe_{0.975}Ni_{0.025}Rh$ . A very large effective refrigerant capacity of 492.8 J kg<sup>-1</sup> with the hot end of the refrigerator at 307.1K and the cold end at 230.5K has been achieved [39]. This is probably the highest known refrigerant capacity for any material world-wide working at room temperature.

### 9. Glassy Dynamics Across First Order Transition

So far we have seen the influence of disorder on the first order phase transition and how the functional properties, especially their repeatability, depend on the history effects that arise as a result of disorder. The disorder can be used to tune the transition parameters like the onset temperatures and the width of the transition to achieve the desired functionality. However, increasing the disorder may not always tune the desired properties in a monotonic manner but can lead to an entirely new phenomenon.

We now present the results of magnetization relaxation measurements and thermomagnetic history effects across the FM to AFM transition in  $Fe_{0.955}Ni_{0.045}Rh$ . The higher concentration of Ni appears to have an effect of arresting the kinetics of the first order FM to AFM phase transition. This kinetic arrest of the first order phase transition gives rise to a glass-like nonequilibrium state [40]. Fig. 11

shows magnetization as a function of temperature in an applied field of 10 mT under different thermomagnetic histories.



# Fig. 11. Magnetization of Fe<sub>0.955</sub>Ni<sub>0.045</sub>Rh as a function of temperature in a field of 10 mT. Inset shows the thermomagnetic irreversibility on an expanded scale at lower temperatures.

In the zero-field-cooled (ZFC) protocol, the sample is cooled from above 300 K to the lowest temperature in zero field. The field is then switched on and magnetization is measured during warming up the sample. After reaching above 300 K, the magnetization is measured while cooling the sample unidirectionally without switching off the field. This measurement protocol is known as field-cooledcooling (FCC). Once the lowest temperature is reached during the FCC, the sample is warmed up again in the same constant applied field. The resulting M-T curve is denoted as the field-cooledwarming (FCW) curve. The rise in magnetization at around 180 K (see inset of fig. 11) in the ZFC curve, marks the onset of the transition from the AFM to the FM phase. On cooling from above 300 K there is a marked hysteresis across the transition, which is typical of a first order transition. On further cooling down to the lowest temperature, we observe that the transition is not complete and the FCC magnetization curve does not merge with the ZFC magnetization curve (see inset of fig. 11). The FCC magnetization curve would have merged with the ZFC magnetization curve in the event of completion of the FM to AFM transition. This thermomagnetic irreversibility (TMI) gives the first indication that the kinetics of the FM to AFM transition are arrested [41, 42]. However, such TMI between the ZFC and FCC magnetization curves can also arise in case of a spin glass [43] and in case of systems with long range ferromagnetic order [44]. However, the possibility of a spin glass transition or ferromagnetic impurity is ruled out in the present system as the TMI further increases with increase in applied field [40] (results not shown here for the sake of conciseness). This nature of TMI is clearly opposite to the trend observed in case of spin glass [45] and ferromagnets [44] It has been shown that such thermomagnetic history effects are the outcome of the kinetics of the first order transition getting arrested by the application of magnetic field [45], resulting in a magnetic-glass.

We now focus on the kinetics of the ferromagnetic to antiferromagnetic transition in the  $Fe_{0.955}Ni_{0.045}Rh$ alloy during the FCC protocol in a field of 5T, by observing the time dependent magnetization at certain temperatures. At higher temperatures, i.e. near the FM to AFM transition while cooling, the relaxation can be described by the following power law [40]:

$$M(T) / M_0 = -1 + 2t^{\gamma}$$
 (6)

However, at lower temperatures, when the AFM phase has formed in sufficient quantities, the relaxation cannot be explained in terms of a single simple equation. The relaxation is described with a combination of the following laws [40]:

$$A_{1}(T)(-1+2t^{\gamma}) + A_{2}(T)(\exp[(-t/\tau)^{\beta}]$$
 (7)

The second term is the stretched exponential function with  $\beta$  which ranges between 0.6 to 0.9 and  $\tau$  is the time constant.  $A_1(T)$  and  $A_2(T)$  are the temperature dependent weight factors for the power law and stretched exponential parts of equation. The stretched exponential function is a characteristic of glassy dynamics [46] and has been used earlier for explaining the time dependence of magnetization observed during the formation of magnetic-glass in various systems like doped CeFe2 alloys [41] NiMnIn based off-stoichiometric Heusler alloys [47] and Gd<sub>5</sub>Ge<sub>4</sub> [48]. The power law represents the relaxation in the crystalline phase [40].

Fig. 12 shows a relaxation measurements at one representative temperature. The time dependence of magnetization can be fitted with equation 7. The relative weights,  $A_1(T)$  and  $A_2(T)$  are found at various temperatures to see how the transformation proceeds with temperature.



Fig. 12. Time dependence of magnetization of  $Fe_{0.955}Ni_{0.045}Rh$  during the FCC protocol in 5T field at one representative temperature. Thesolid line is a fit to equation 7.



# Fig. 13. The relative phase fractions of the non-arrested and arrested phases across the ferromagnetic to antiferromagnetic transition in $Fe_{0.955}Ni_{0.045}Rh$ during the FCC protocol at 5T.

A plot of  $A_1$  and  $A_2$  as a function of temperature in fig. 13 gives a qualitative picture of how the crystalline and glassy phases evolve with temperature out of the unconverted FM phase. It can be seen that the glassy dynamics appear just below 110 K, after a substantial amount of FM phase has already been converted to the equilibrium AFM state. It can be inferred that the growth of the product phase (AFM in this case) itself influences the arrest of the kinetics of the FM to AFM transition [40]. The glassy phase thus seems to be an outcome of the disorder influenced nucleation and growth dynamics across the first order transition.

Liquids which undergo glassy transitions are categorized as strong or fragile depending on the how the viscosity or the time constant of the stretched exponential varies with temperature [46] With analogy to this framework, in our case the liquid state corresponds to the ferromagnetic phase. The temperature dependence of follows the Arhenius function given by:

$$\tau = A \exp(E / K_B T) \tag{8}$$

where *E* is the activation energy and  $K_B$  is the Boltzmann constant. Figure 14 shows the temperature dependence of  $\tau$  in the stretched exponential term of equation 7 along with the fit to equation 8. The Arhenius functionality of the time constant indicates that the ferromagnetic phase behaves as a strong glass forming liquid.



Fig. 14. The temperature dependence of the time constant  $\tau$  in the stretched exponential term of equation 7. The solid squares are the experimental data. The solid line is a fit to the data using equation 8.

### **10.** Conclusion

In conclusion, we have studied the nucleation and growth dynamics across the disorder influenced first order magneto-structural transition in Fe-Rh based alloy system. The thermomagnetic history effects arising due to phase coexistence across this transition are shown to influence the response of the material for multiple temperature and magnetic field cycles. A reproducible magneto-caloric effect with a large refrigerant capacity at room temperature could be achieved by understanding these history effects. The disorder is not only important in tuning the functionality in alloys, but also can lead to an entirely new phenomenon like the kinetic arrest of the phase transition.

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### KINETICS OF PHASE TRANSFORMATION IN METALLIC GLASSES

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### 1. Introduction

Amorphous materials are the materials without shape ("A" means without and "morphe" means shape in Greek language). They lack long range order and anisotropic properties of crystals. Amorphous solids possess short range periodicity at atomic level and all the properties of these solids are isotropic in nature. A reversible transition in these materials from solid to liquid phase, that involves conversion of a hard and brittle state into a relatively soft rubber like state, is known as glass-liquid transition (or glass transition). An amorphous material that exhibits a glass transition can be termed as glass. Conversion of a liquid to a glass comprises of cooling of the melt such that its liquid like structure remains intact, which results in decrease in viscosity of the melt by many orders of magnitude. Generally amorphous solids include polymers, thin films, nanostructured materials, etc.

Metallic alloys are crystalline in nature, i.e., they possess long range order and are anisotropic in nature. Metallic alloys can be converted into glasses by cooling their melt at a rate high enough to suppress their crystallization. These supercooled metallic alloys with a disordered atomic scale arrangement are known as "**metallic glasses**". Structurally, metallic glasses are non-crystalline with short range order, but they possess properties of metals such as good electrical conductivity, ductility, strength, oxidative stability, etc. According to Inoue [1] the formation of metallic glasses can be enhanced even at lower cooling rates by: a) increasing the number of components, b) size mismatch between the components, and c) negative heat of mixing. The presence of different constituent metals or metalloids, of different sizes, in metallic alloy allows them to transform into a disordered structure. A greater number of constituents (more that three) of different sizes lead to lower free volume (greater viscosity) of metallic alloy in molten state, and hence allowing its formation even at lower cooling rates. The atoms of the alloys face a barrier to form an ordered structure due to the increased viscosity and hence they get frozen into a glassy state. The different sized components of metallic glass also lead to the formation of a better wear and corrosion resistant material without any plastic deformation. With a significant difference in atomic radius (greater than 12 %) of the components of metallic glass, a high packing density and lower free volume can be achieved. A negative heat of mixing among the components increases the stability of the supercooled liquid phase by inhibiting crystal nucleation.

Among the various methods of preparation of metallic glasses, melt spinning and melt quench casting are the most famous methods. Melt spinning method allows the formation of metallic glass ribbons, whereas melt quenching method is used for the formation of metallic glasses in bulk. Metallic glasses with thickness greater than 1 mm are termed as "**bulk metallic glasses (BMGs)**". Other methods of metallic glass synthesis are physical vapor deposition (PVD), solid state reactions, mechanical alloying, ion irradiation, sputtering, etc.

Right from the formation of first metallic glass of Au<sub>75</sub>Si<sub>25</sub> by Duwez [2], the investigations of structure, properties, and different methods of synthesis of metallic glasses have been a matter of significant interest for material researchers due to their potential applications in various scientific and engineering disciplines. The first BMG was Pd–Cu–Si alloy prepared by Chen in 1974 [3], followed by the formation of Pd–Ni–P BMG by Turnbull et al. [4, 5]. Inoue et al. found another group of good glass formers; rare earth based alloys, i.e., La–Al–Ni and La–Al–Cu [6]. Successively, families of Mg-based and Zr-based metallic glasses such as Mg–Y–Cu, Mg–Y–Ni, Zr–Cu–Ni, Zr–Cu–Ni–Al BMGs etc., were also developed [7, 8].

On application of thermal treatment, metallic glasses undergo change in their structure i.e., from amorphous metastable state to a stable crystalline state followed by melting of alloy. The properties of amorphous alloys are entirely different from their corresponding crystalline phase. This makes the study of thermally activated phase transformations significant. The crystallization of metallic glasses involves nucleation and growth of nuclei. Nucleation is a rapid process as compared to growth. One of the most widely used thermo-analytical technique for studying the kinetics of crystallization of metallic glass is the differential scanning calorimetry (DSC). DSC enables us to study the crystallization process in metallic glass, by providing data of crystallized fraction with temperature or time. Both isothermal and non isothermal conditions can be used in DSC for studying crystallization kinetics [9-13]. Modulated DSC (MDSC) is a more improvised version of DSC, which overcomes most of its disadvantages. But, only few studies are available in literature [14-15] on study of crystallization kinetics of metallic glasses using MDSC.

The analysis of data procured from DSC experiments can be done in two ways, isokinetic and iso conversional. A single value of kinetic parameters such as activation energy is obtained by isokinetic methods, since they assume the transformation mechanism to be same throughout the temperature or time range. On the other hand, an isoconversional method assumes the transformation mechanism at a constant degree of conversion as a function of temperature and provides kinetic parameters varying with the degree of conversion,  $\alpha$ . Generally, multi-component metallic glasses crystallize in multiple steps; their transformation mechanism cannot be considered to be the same throughout the process. Different mechanisms may be involved for different steps. Thus, selection of correct method to study crystallization behavior of metallic glasses is a major issue. Many researchers [16-19] have studied crystallization kinetics by various isokinetic and isoconversional methods. Recently, Lu and Li [20] have used various isokinetic and isoconversional methods for studying the kinetics of non-isothermal crystallization in Cubased metallic glasses. Some others researchers, such as Wu et al. [21] and Svoboda and Malek [22], have considered that isoconversional methods are sufficient for the study of crystallization kinetics.

### 2. Theoretical Background

The reaction rate for non iso-thermal crystallization kinetics can be expressed by the following kinetic equation [23]:

$$\frac{d\alpha}{dT} = \frac{1}{\beta}k(T)f(\alpha) = \frac{k_0}{\beta}\exp\left(-\frac{E}{RT}\right)f(\alpha) \qquad (1)$$

Where, k(T) is rate constant,  $\beta$  is heating rate,  $\alpha$  is degree of conversion, and  $f(\alpha)$  is characteristic function of the reaction model.

From equation (1), it is clear that the reaction rate depends both on reaction model function,  $f(\alpha)$  and the rate constant k(T). The determination of kinetic parameters  $k_o$ , E and  $f(\alpha)$  is the chief aim of studying kinetics of crystallization. Various isoconversional and isokinetic methods are available in literature [24-34] for the determination of the kinetic triplet.

### Iso-conversional methods

Isoconversional methods are independent of reaction model  $f(\alpha)$ , and hence they are also known as model free methods. Further, model free methods are classified as linear integral and linear differential methods. Integral isoconversional methods depend on the approximation of the temperature integral. Kissinger–Akahira–Sunose (KAS) [24-26], Kissinger [24], Augis and Bennett [27], Bosewell [28], Ozawa–Flynn–Wall (OFW) [29-30], etc methods come under this category. Differential isoconversional methods are based on the rate of transformation [31-32]. Methods derived by Friedman [31] and Gao and Wang [32] are differential isoconversional methods.

Separation of variables and integration of equation (1) gives:

$$g(\alpha) = \int_{0}^{\alpha} [f(\alpha)]^{-1} d\alpha = \frac{k_0}{\beta} \int_{0}^{T} \exp\left(-\frac{E}{RT}\right) dT \quad (2)$$

Above integral equation doesn't have an exact analytical solution, hence various approximations of this integral are suggested in literature [35-39]. Activation energies are evaluated at different stages of conversion,  $\alpha$ .

The general form of the linear equation expressing the linear integral based on iso-conversional methods is [40]:

$$\ln\left(\frac{\beta}{T_{\alpha}^{k}}\right) = -A\frac{E_{\alpha}}{RT_{\alpha}} + C$$
(3)

Where the parameters k and A are dependent on approximations of temperature integral, C is constant and the subscript  $\alpha$  designates the degree of conversion. For Ozawa-Flynn-Wall (OFW) model, k=0, A=1.0516, and for Kissinger-Akahira-Sunose (KAS) model, k=2, A=1, etc.

### Isokinetic methods

These methods are model fitting methods that depend upon the consideration of various kinds of models for the determination of kinetic parameters E and  $k_0$ . Isokinetic methods are, in general, employed to study the kinetics of phase transformations occurring in isothermal conditions. Most of the isokinetic methods are based on the KJMA rate equation [41-45], given by

$$\frac{d\alpha}{dt} = nk(1-\alpha) \left[ -\ln(1-\alpha) \right]^{(n-1)/n}$$
(4)

Where  $\alpha$  is degree of conversion at a particular time, *n* is Avrami (growth) exponent and *k* is the rate constant given by

$$k(T) = k_0 \exp\left(-\frac{E}{RT}\right)$$
(5)

Where  $k_0$  is pre-exponential factor, E is the activation energy and R is the universal gas constant.

From equations (4) & (5) transformed fraction can be expressed as

$$\alpha = 1 - \exp\left[-\frac{k_0}{\beta} \int_{T_0}^T \exp\left(-\frac{E}{RT}\right) dT\right]^n$$
 (6)

The integral in eq. (6) does not have an exact solution and hence one has to switch to approximations. Various approximations have been used in literature to obtain an accurate solution of the integral [46-48]. A simple and satisfactorily accurate solution of the exponential integral in the non-isothermal kinetic equation for linear heating can be obtained by using Gorbachev approximation [48] i.e., eq. (7).

$$\int_{0}^{T} e^{-E/RT} dT = \frac{RT^{2}}{E + 2RT} e^{-E/RT}$$
(7)

Adopting this approximation, in Eq. (6),

$$\alpha = 1 - \exp\left[-\left\{\frac{k_0 R T^2}{\beta(E + 2RT)} \exp\left(-\frac{E}{RT}\right) dT\right\}^n\right] \qquad (8)$$

The values of *E*, *n* and  $k_0$  can be determined by fitting the experimental data of  $\alpha$  to eq. (8) with the help of method of least square.

### 2. Results and Disscussions

Under the application of thermal treatment, a metallic glass undergoes crystallization process before it melts. A multi-component metallic glass may crystallize in multiple steps, depending upon the crystallization temperature of its components. Both, isoconversional and isokinetic methods can be used to analyze the crystallization process in metallic glasses. Patel at al [16] have performed the analysis of crystallization kinetics of first peak for Zr<sub>52</sub>Cu<sub>18</sub>Ni<sub>14</sub>Al<sub>10</sub>T<sub>i6</sub> metallic glass by different isokinetic and isoconversional methods. But, the validity of a model must be verified before applying it for studying crystallization kinetics. Therefore, in present study, we have tested the validity of different models by various techniques, and then analyzed the kinetic process by different isokinetic and isoconversional methods. Among the various testing techniques the most prior one is the leastsquare fitting of the experimental data of fractional crystallization by eq. (8). The initial estimates of E and  $k_0$  can be obtained from Kissinger equation. Table 1 reports the values of Avrami (growth) exponent (n), pre-exponential factor  $(k_0)$ , and activation energy (E)obtained by least square fitting of fractional crystallization data for first crystallization peak of  $Zr_{52}Cu_{18}Ni_{14}Al_{10}Ti_6$  metallic glass.

Table 1 Values of Avrami (growth) exponent (n), pre-exponential factor  $(k_0)$ , and activation energy (E) obtained by least square fitting of fractional crystallization data for first crystallization peak

Table 1. Values of Avrami (growth) exponent (n), pre-exponential factor  $(k_{\theta})$ , and activation energy (E) obtained by least square fitting of fractional crystallization data for first crystallization peak

Heating Rates (°Cmin <sup>-1</sup> )	KJMA			
	n	$k_{\theta}$ (s <sup>-1</sup> )	E (kJmol <sup>-1</sup> )	
5	1.27	8.00 x 10 <sup>22</sup>	327	
10	1.35	$7.00 \ge 10^{22}$	315	
15	1.46	6.68 x 10 <sup>22</sup>	325	
20	1.49	6.00 x 10 <sup>22</sup>	324	

A good fitting of experimental data indicates the validity of KJMA model for the study of kinetics process. Figure 1 represents the fitting of experimental data of crystallized fraction, as a function of temperature, for  $Zr_{52}Cu_{18}Ni_{14}Al_{10}Ti_6$  metallic glass at different heating rates for peak- 1. Figure 1 clearly indicates that in the range  $0.2 < \alpha < 0.8$  the theoretical values of  $\alpha$  calculated using eq (8) exactly fits the experimental data. Below  $\alpha = 0.2$  and above  $\alpha = 0.8$ , a small mismatch between theoretical and experimental data may have arisen due to an error in baseline correction at tails of the crystallization peak.



Fig. 1. crystallized fraction as a function of temperature at different heating rates for peak-1for  $Zr_{52}Cu_{18}Ni_{14}Al_{10}Ti_6$  metallic glass. Symbols represent experimental points and solid lines show the least square fitted curve using eq. (8)

Another method, proposed by Malek [49-50], involves the calculation of functions  $z(\alpha)$  and  $y(\alpha)$ . If the maximum of the function  $z(\alpha)$  comes in the range (0.61-0.65), then KJMA model can be used for applicable model. In present study we have calculated both  $y(\alpha)$  and  $z(\alpha)$  as expressed below:

$$w(\alpha) = \phi \exp(E/RT)$$
 (9)

$$z(\alpha) = \phi T^2 \tag{10}$$

Where  $\varphi$  is the heat flow evaluated during the crystal growth, represented by the following equation

$$\phi = \Delta H_c k_0 \exp(-E/RT) f(\alpha) \tag{11}$$

And

$$f(\alpha) = n(1-\alpha) \left[ -\ln(1-\alpha) \right]^{(n-1)/n}$$
 (12)

Where,  $\Delta H_c$  is the enthalpy difference associated with crystallization process. The maximum value of  $y(\alpha)$  and  $z(\alpha)$  are denoted by  $\alpha_M$  and  $\alpha_P$  respectively. Figure 2 represents the variation of  $y(\alpha)$  and  $z(\alpha)$ with crystallized fraction  $\alpha$ . As shown in the plots,  $\alpha_P$ falls in the range (0.42 - 0.53), whereas  $\alpha_M$  falls in the range (0.15 – 0.24) for peak 1. These values are less than that predicted by Malek. Hence in present case, KJMA model cannot be used for the study of nonisothermal crystallization kinetics.



Fig. 2. Normalized  $y(\alpha)$  and  $z(\alpha)s$  with crystallized fraction  $\alpha$  for different heating rates

If  $0 < \alpha_M < \alpha_P$ , and  $\alpha_P$  is not equal to zero, then Malek's criteria suggests the equation for  $f(\alpha)$  given by Sestak-Berggren [51], used for evaluating the kinetic parameters.

Sestak-Berggren equation is given as:

$$f(\alpha) = \alpha^{M} (1 - \alpha^{N})$$
 (13)

Where, M and N are kinetic parameters, their ratio can be calculated as:

$$\frac{M}{N} = \frac{\alpha_M}{(1 - \alpha_M)} \tag{14}$$

Considering S-B equation, the reaction rate can be given as:

$$\frac{d\alpha}{dt} = Z \exp\left(-\frac{E_{\alpha}}{RT}\right) \alpha^{M} (1-\alpha)^{N}$$
 (15)

Another way of representing SB equation is:

$$\ln\left[\left(\frac{d\alpha}{dt}\right)\exp\left(\frac{E_{\alpha}}{RT}\right)\right] = \ln Z + N\ln\left[\alpha^{M/N}(1-\alpha)\right]$$
(16)

The value of N can be obtained from the slope of the plot  $\ln[(d\alpha/dt) \exp(E_{\alpha}/RT)]$  versus  $\ln [\alpha^{MN}(1-\alpha)]$ . The parameter M can then be calculated from equation (14). In present case, the values of the kinetic parameters M and N are calculated by SB method, and the established reaction models at different heating is reported in Table 2.

Heating Rates (°Cmin <sup>-1</sup> )	f(a)
5	$\alpha^{0.21}(1-\alpha)^{0.94}$
10	$\alpha^{0.18}(1-\alpha)^{1.02}$
15	$\alpha^{0.37}(1-\alpha)^{1.16}$
20	$\alpha^{0.35}(1-\alpha)^{1.11}$

For a more precise check of the above determined kinetic parameters, Master plot and heat flow curve match can be performed. In master plot method [52], considering  $\alpha = 0.5$ , the experimental and theoretical values of the appropriate reaction model can be compared by applying the following equation:

$$\frac{f(\alpha)}{f(0.5)} = \frac{d\alpha/dt}{\left(\frac{d\alpha}{dt}\right)_{0.5}} \frac{\exp\left(\frac{E_{\alpha}}{RT}\right)}{\exp\left(\frac{E_{\alpha}}{RT}\right)}$$
(17)

The left side of the expression represents the theoretically calculated reduced reaction model with respect to the reaction function at  $\alpha = 0.5$ . The right side of the expression is calculated from the experimentally determined values of activation energy. A close match between the reduced theoretical and experimental results indicates that the reaction model used is appropriate for studying the crystallization kinetics. Figure 3 shows a good match of both curves, except for a small variation near peak values. Hence, in present case SB equation can be considered to be a good reaction model for crystallization kinetics study.



Fig. 3. Master plot at the heating rate of  $10^{\circ}$  C min<sup>-1</sup>

The theoretical normalized heat flow curves can be obtained by making use of calculated kinetic parameters i.e., *E* and *n* and equations (11) and (12). Figure 4 represent the experimental normalized heat flow and the theoretically calculated normalized heat flow using equations (11) and (12). Both the reaction models for  $f(\alpha)$  i.e., JMA and SB, are tested and values of E, n, and  $k_0$  used, are those obtained from the least square fitting method and are listed in table 1. This method, very effectively, provide the correct information about the method applicable for studying crystallization kinetics of metallic glasses. The information about the kinetic parameters can then be drawn by using suitable methods i.e., isokinetic or isoconversional. As indicated by Fig. 4, initially JMA model lies close to the experimental heat flow curve. But as temperature increases and reaches its peak value, SB model is found to match well with the experimental heat flow curve till the end of the peak. It indicates that both models tested here, can satisfactorily explain the kinetics of crystallization for metallic glasses to a certain extent. Since crystallization process changes with temperature, one may need to switch to different models for studying the kinetic process at different stages of the crystallization event. Hence, moving towards model free methods seems to be a better approach for studying the kinetic process.



## Fig. 4. Normalized heat flow curves at 10<sup>0</sup> C min<sup>-1</sup>; ( ) experimental, (- - -) SB model results, (--) JMA model

### Isoconversional methods:

1

### Linear integral iso-conversional methods Kissinger-Akahira-Sunose (KAS) method:

Kissinger-Akahira-Sunose (KAS) [24-26] used the approximation given by Coats and Redfern [26] to evaluate the integral in Eq. (2), and hence derived the following equation:

$$n\left(\frac{\beta}{T_{\alpha}^{2}}\right) = -\frac{E_{\alpha}}{RT_{\alpha}} + \ln\left(\frac{k_{0}R}{E_{\alpha}}\right)$$
(18)

The slope and intercept of  $\ln (\beta/T_{\alpha}^{2})$  vs.  $1000/T_{\alpha}$  plot provides the values of  $E_{\alpha}$  and the  $k_{0}$  for constant conversion,  $\alpha$ . Fig 8 shows KAS plot for  $\alpha$  =0.5, and the variation of  $E_{\alpha}$  with  $\alpha$  is shown in Fig. 8.



### Fig. 5. KAS plot for $\alpha = 0.5$

**Kissinger method:** Kissinger equation is based on the assumption that the rate of reaction is highest at peak temperature  $(T_p)$ . It calculates activation energy at a constant degree of conversion,  $\alpha$  i.e., at  $T_{\alpha} = T_p$  only.

$$\ln\left(\frac{\beta}{T_p^2}\right) = -\frac{E}{RT_p} + \ln\left(\frac{k_0R}{E}\right)$$
(19)

The slope and intercept of the  $\ln (\beta/T_p 2)$  vs.  $1000/T_p$ plot, gives the values of activation energy (*E*) and the pre-exponential factor ( $k_0$ ) respectively. The value of *E* and  $k_0$  is given in Table 3.

Augis & Bennett's method: This method introduces a modification in Kissinger equation. Apart from peak temperature  $(T_p)$  it also incorporates onset temperature of crystallization  $(T_p)$ [27].

$$\ln\left(\frac{\beta}{\left(T_{p}-T_{o}\right)}\right)=-\frac{E}{RT_{p}}+\ln\left(k_{0}\right)$$
(20)

The values of *E* and  $k_0$  calculated respectively from the slope and intercept of the plot  $\ln (\beta / (T_p - T_o))$  vs.  $1000/T_p$  are given in Table 3.

### Table 3. Activation energies (E) and preexponential factor $(k_a)$ for different methods [16]

Methods	E (kJmol <sup>-1</sup> )	$k_{\theta}$ (sec <sup>-1</sup> )	
Kissinger	$259\pm2$	4.86 x 10 <sup>17</sup>	
Augis & Bennett	271 ± 1	3.33 x 10 <sup>18</sup>	
Boswell	$256\pm2$		
Ozawa	$258 \pm 2$		
Gao & Wang	$278 \pm 3$		

**Boswell method:** Boswell method [28] was formulated to overcome the limitations of Augis and Bennett method. As  $((T_p - T_0)/T_p) \approx 1$ , Augis and Bennett methods may provide crude results.

$$\ln\frac{\beta}{T_p} = -\frac{E}{RT_p} + const$$
 (21)

The value of *E* as calculated from the slope of the plot  $\ln(\beta/T_p)$  vs.  $1000/T_p$  is 256 kJ/mol for peak-1. The value is given in Table 3.

### Ozawa-Flynn-Wall (OFW)

Ozawa-Flynn-Wall [29-30] solved eq. (2) by using Doyle's approximation [53-55]. The OFW expression is

$$\ln \beta = -1.0516 \frac{E_{\alpha}}{RT_{\alpha}} + const \qquad (22)$$

The plot  $\ln \beta$  vs.  $1000/T_{\alpha}$  for constant conversion ( $\alpha$ ) is shown in Fig. 6 for peak 1. The variation of *E*, calculated from OFW method, with  $\alpha$  is shown in Fig. 8. At peak crystallization temperature i.e.,  $T_{\alpha} = T_{p}$ , the value for activation energy is determined using Ozawa method [29]. This method involves the substitution of  $T_{p}$  for  $T_{\alpha}$  in equation (22). Table 3 reports the value of *E* obtained by Ozawa method.



Fig. 6. OFW plot for  $\alpha = 0.5$ 

### Linear differential iso-conversional methods

### Friedman method:

Friedman [31] derived an expression for estimation of activation energy of crystallization based on the differential of the transformed fraction. Since it does not require any approximation for temperature integral, accurate results of E are expected to be obtained. The expression given by Friedman is as follows:

$$\ln\left(\frac{d\alpha}{dt}\right)_{\alpha} = \ln\beta\left(\frac{d\alpha}{dT}\right)_{\alpha} = -\frac{E_{\alpha}}{RT_{\alpha}} + \ln\left(k_0f(\alpha)\right) \quad (23)$$

However, since it is a differential method its accuracy is limited by signal noise. Fig. 7 represents Friedman plot for  $\alpha = 0.5$ . The values of *E* calculated from the slope of the plot  $\ln (\beta (d\alpha/dT)_{\alpha})$  vs.  $1000/T_{\alpha}$  for different conversion,  $\alpha$  are shown in Fig. 8.



### Fig. 7. Friedman plot for $\alpha = 0.5$

A special case of Friedman method, which invovles the determination of E only at  $T_p$  was suggested by Gao & Wang [32]. The expression used by Gao & Wang is:

$$\ln\left(\beta\frac{d\alpha}{dT_p}\right) = -\frac{E}{RT_p} + const$$
 (24)

The values of *E* can be calculated from the slope of the plot  $\ln (\beta (d\alpha/dT_p))$  vs.  $1000/T_p$ . The values are given in Table 3.



## Fig. 8. Local activation energy E at different α from different methods [16]

As observed from the figure 8, both KAS and OFW methods provide the values of local activation energy of crystallization close to each other, whereas the values of  $E_a$  obtained by Friedman method is quite scattered. Moreover, the values of  $E_{a}$  slowly increase with the crystallized fraction  $\alpha$ , as calculated by KAS and OFW methods. This increase in  $E_a$  may be due to the increase in energy barrier for atomic diffusion. Growth of crystal nuclei requires diffusion of components of alloy through the super cooled liquid. The energy barrier required to be overcome for atomic diffusion increases due to the large size mismatch and bonding between the various components of the alloy, and atomic diffusion required for growth of the nuclei becomes difficult. Hence, the values of  $E_a$  are supposed to increases with  $\alpha$ . This increase in  $E_{\alpha}$  also indicates that even before first crystallization step ends, the second step starts.

### **Isokinetic Methods**

### Matusita and Sakka method:

Matusita and Sakka [33] gave the following expression for studying the non isothermal crystallization kinetics of metallic glasses.

$$\ln[-\ln(1-\alpha)] = -n\ln\beta - \frac{mE}{RT} + Const \qquad (25)$$

Where the integer *m* defines the dimensionality of the crystal and the Avrami exponent *n* gives information about the nucleation process. The value of *n* can be obtained from the slope of the plot of  $\ln[-\ln(1-\alpha)]$  versus  $\ln\beta$  (Fig. 9), at a constant temperature. Further, the slope of the plot  $\ln[-\ln(1-\alpha)]$  versus 1/T (Fig. 10) at a constant heating rate gives the value of *m*.



Fig. 9. Plot of  $\ln[-\ln(1 - \alpha)]$  vs.  $\ln \beta$ 



Fig. 10. Plot of  $\ln[-\ln(1-\alpha)]$  vs.  $1000/T@\,15^{\circ}\,\mathrm{C\,min^{-1}}$ 

### Modified Kissinger method:

The modified Kissinger equation [34] is expressed as:

$$\ln\left(\frac{\beta^n}{T_p^2}\right) = -\frac{mE}{RT_p} + Const$$
 (26)

The slope of  $\ln(\beta^n/T_p^2)$  versus  $1/T_p$  gives the value of activation energy of crystallization. In this approach, the determination of the parameters *m* and *n* becomes important for determination of *E*. The value of *n* is obtained from Matusita and Sakka method.



Fig. 11. Modified Kissinger plot for *n* = 2.66 [16]

### 3. Conclusion

The crystallization kinetics of Zr-based metallic glass has been studied by both model dependent isokinetic and model-free isoconversional methods. The applicability of various model have been checked for studying the kinetic process. The normalized heat flow curves obtained by both SB and JMA models were found to be in good agreement with the experimental heat flow curve. Before peak JMA model was found to lay closer to experimental data, whereas after peak SB model matches well with the experimental heat flow curve. So, in order to avoid switching to different models at different stages of crystallization process, isoconversional methods (model free) seems to be a better choice for studying crystallization kinetics of metallic glasses. Moreover, the isokinetic methods, though model dependent, provide single value of activation energy together with Avrami exponent n,

which gives an idea about the dimensionality of the growth of crystals. Isoconversional techniques, on the other hand, provide quite accurate values of  $E_a$  as a function of  $\alpha$ . The results obtained through KAS, OFW methods indicate that activation energy increases with  $\alpha$ . This increase may be due to increase in energy barrier required for diffusion of atoms towards the nuclei, leading to growth of crystals.

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### **REVIEW ON THERMAL CHARACTERIZATION OF POLYMER NANOCOMPOSITES**

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### Abstract

This article describes the thermal characterization of polymer nanocomposites through transient plane source (TPS) technique, dynamic mechanical analysis (DMA) and differential scanning calorimetry (DSC). The TPS method is precise and convenient method for measuring the thermal transport properties (i.e Thermal conductivity and Thermal diffusivity) of conducting and non-conducting materials. DMA is used to measure the thermomechanical properties of polymer nanocomposites. On the other hand, DSC provides useful information about the phase transformation occurring in samples. This article also presents some important results of thermal conductivity, thermo-mechanical and thermodynamic properties of some of the polymer nanocomposite materials.

### 1. Introduction

Thermal characterization is a study in which physical property of a material is measured by controlled temperature program. The changes in the properties of the material by heating could result from purely physical phenomena such as melting, vaporization or polymorphic transformations to chemical processes such as thermal decompositions of materials, oxidation of metals and alloys, reduction of solid metal oxides, etc. All physical or chemical changes resulting from heating are accompanied by energy changes. However, other properties such as mass, dimension, modulus of elasticity, conductivity etc. may also undergo concurrent changes on heating. Each of the thermal characterization techniques is identified with the property measured as a function of temperature. Some of the commonly used thermal characterization techniques are thermogravimetry (TG), differential thermal analysis (DTA), differential scanning calorimetry (DSC), dynamic mechanical analysis (DMA), thermal constant analysis (TCA) etc. Table 1 provides the list of the experimental parameters measured from the above mentioned characterization techniques.

## Table 1. Classification of thermal techniques withthe property measured

Technique	Abbre- viation	Physical Property Measured
Thermo- gravimetry	TG	Mass/change in mass of the sample
Differential Thermal Analysis	DTA	Difference in temperature between the sample and a thermally inert reference material heated identically
Differential Scanning Calorimetry	DSC	Rate of change of enthalpy
		Contd

Technique	Abbre- viation	Physical Property Measured
Dynamic Mechanical Analysis	DMA	Change in visco- elastic properties under oscillatory load
Thermal Constant Analysis	TCA	Thermal conductivity, Thermal diffusivity

When a material or a system is given heat energy, then the propagation of the energy from one end to other and the interaction of matter with heat could be correctly predicted by the experimental values of some of the thermal properties listed below:

- Thermal conductivity
- Thermal diffusivity
- Specific heat
- Thermal expansion
- Thermo elasticity
- Phase transformations

Based on this, we will focus our attention on the thermal characterization of materials through thermal constant analysis (also known as transient plane source technique), dynamical mechanical analysis and differential scanning calorimetry.

### 2. Transient Plane Source (TPS) Technique

TPS technique is a device that can be used both in laboratory and in-situ measurements of all the three (thermal conductivity, thermal diffusivity and specific heat) related properties from cryogenic to high temperatures (1000 K). It can measure thermal conductivities between 0.01 and 500 W/mK. The motive behind the development of the TPS technique has been:

- (i) to cover as large range of the transport properties as possible
- (ii) to cover a large number of materials
- (iii) to achieve maximum convenience by the use of a resistive element both as heat source and temperature sensor
- (iv) maximum applicability

Transient plane source method, which is an extension of the transient hot strip method was introduced by Gustafsson as the modified version of THS in 1989. Schematic diagram of TPS sensor is shown below in Fig.1.



### Fig.1. TPS sensor

TPS sensor consists of an electrically conducting pattern in the form of a bifilar spiral. This conducting pattern has been etched out of a thin metal foil (0.01mm thick), whose electrical resistivity is known as a function of temperature. This spiral has been sandwiched between thin insulating sheet of kapton (0.04 mm) or mica depending upon their use in low, room and high temperature ranges, respectively. The plane disc sensor is placed between two identical plane surfaces of the samples, so as to obtain good thermal contact and then heated (typical temperature rise  $\sim 0.5$  to 1K) by an electrical current for a short period of time while the voltage increase over the sensor is recorded.

### 2.1 Theory of Transient Plane Source Technique

The TPS method has proved to be a precise and convenient method for measuring the thermal transport properties of conducting and nonconducting materials. The TPS method consists of an electrically conducting pattern, which serves both as source of heat given to the material and as a sensor of temperature increase in the sample. Assuming the conducting pattern to be in y-z plane of a co-ordinate system, the rise in the temperature at a point y-z at time t due to an output power per unit area Q is given by [1]

$$\Delta T(y,z,\tau) = \frac{1}{4\pi^{3/2} a\lambda} \int_{0}^{\tau a} \sigma^{-2} d\sigma \int_{A} dy' dz' Q$$

$$\left(y',z',t - \frac{\sigma^{2} a^{2}}{\chi}\right) \exp\left[-\frac{(y-y')^{2} + (z-z')^{2}}{4\sigma^{2} a^{2}}\right] \qquad (1)$$

where

 $\chi$  (t-t') =  $\sigma^2 a^2$   $\theta = a^2 / \chi$ 

and 
$$\tau = [t/\theta]^{1/2}$$
 (2)

a is the radius of the hot disc (source and the sensor) which gives a measurement of the overall size of resistive pattern and  $\theta$  is known as the characteristic time.  $\sigma$  is a constant variable,  $\lambda$  is the thermal conductivity in units of W/mK and  $\chi$  is the thermal diffusivity of the sample in units of m<sup>2</sup>/s. The temperature increase  $\Delta T$  (y, z,  $\tau$ ) because of flow of current through the sensor gives rise to a change in the electrical resistance  $\Delta R$  (t), which is given as:

$$\Delta R(t) = \alpha R_0 \Delta T(\tau) \tag{3}$$

where  $R_0$  is resistance of TPS element before the transient recording has been initiated at room temperature,  $\alpha$  is the temperature coefficient of resistance (TCR) and  $\Delta T(\tau)$  is the properly calculated mean value of the time dependent temperature increase of the TPS element. It is possible to write down an exact solution [2] for the hot disc if it is assumed that the disc contains a number 'm' of concentric rings as sources. From the ring source solution we immediately get

$$\overline{\Delta T(\tau)} = \frac{P_0}{\pi^{\frac{3}{2}} a \lambda} D_s(\tau)$$
(4)

where

$$D_{s}(\tau) = \left[ m(m+1) \right]^{-2} \times \int_{0}^{\tau} \frac{d\sigma}{\sigma^{2}} \left[ \sum_{l=1}^{m} l \right]$$

$$\left\{ \sum_{k=1}^{m} k. Exp\left( \frac{\left(-l^{2}-k^{2}\right)}{2\sigma^{2}m^{2}} \right) \right\} L_{0}\left( \frac{lk}{2\sigma^{2}m^{2}} \right) \right\}$$
(5)

In Eqs. (4) and (5),  $P_0$  is the total output power,  $L_0$  is the modified Bessel function and l, k are the dimensions of the resistive pattern.

The determination of thermal conductivity ( $\lambda$ ) and thermal diffusivity ( $\chi$ ) has been done using the analysis of the U-t curve (Fig. 2) and Eqs. (2) and (4).

TPS sensor, sample holder for room temperature measurement and sample holder for low temperature measurement are shown in following Fig. 3.



Fig. 2. U-t graph for measurement of thermal conductivity and thermal diffusivity



Fig. 3. (a) TPS element, (b) Sample holder (c) Sample holder for low temperature arrangement

### 2.2 Thin Film Measurements

For the measurement of thermal conductivity of thin film with thickness of the order of microns, the experiment is performed in two steps. In the first step, the source of heat and sensor of temperatures is sandwiched between the two samples having smooth surfaces, and then this arrangement is placed between the two auxiliary metal (stainless steel) pieces as shown in the Fig.4.



Fig. 4. Illustration of Thin Film Method



## Fig. 5. Temperature difference across the sample with background material

Data for the temperature increase (shown as green line in Fig.5) over a given time is collected using the software available with the Hot Disk Thermal Constant Analyser TPS 2500S for the purpose.

In the second step, the experiment is repeated with the sensor sandwiched between the same two pieces of the metal and data for the temperature increase (shown as blue line in Fig. 5) is again collected using the above mentioned procedure. Employing these two temperature increase, thickness of the film and power delivered to the sample, the  $\lambda$  can be determined through the following relation:

$$\mathbf{P} = 2 \, \mathbf{A}\lambda \, (\Delta \mathbf{T}/\Delta \mathbf{x}) \tag{6}$$

where, P is total output of power, A is sensor area,  $\lambda$  is the thermal conductivity of the sample,  $\Delta T$  is the fully developed temperature difference across the sample (Fig. 5) and  $\Delta x$  is sample thickness.

### 2.3 Experimental Measurements of Effective Thermal Conductivity of Different Polymer Nanocomposites

The effective thermal conductivity for CdS/PMMA, ZnS/PMMA, CdS/PS, ZnS/PS and CdS/PVC nanocomposites in the form of thin films (thickness  $\approx 0.1$  mm) has been measured using transient plane source (TPS) technique [3-5]. Figures 6-8 show the variation of effective thermal conductivity for CdS/PS, ZnS/PS and CdS/PVC nanocomposites with different nanoparticle concentrations. The variation of effective thermal conductivity with temperature at different fixed weight percentage of CdS (or ZnS) nanoparticles has been discussed in terms of the mean free paths of the phonons. With the increase of temperature, polymeric chains straighten out more and more and the mean free path of phonons increases resulting into an increase in the thermal conductivity up to glass transition temperature [6,7]. Above the glass transition temperature, most of the polymeric chains are straightened out resulting no further increase of thermal conductivity and thus the thermal conductivity becomes constant. It has also been observed that the effective thermal conductivity of nanocomposite increases with the increase of nanoparticles concentration at low wt. % and decreases at higher wt. %. This has been explained on the basis of the existence of thermal resistance developed due to scattering of phonons with interface. It is well known that the polymer has certain free volume in pure form. When CdS (or ZnS) nanoparticles are introduced into polymer, they reduce the free volume resulting into compact structure of composite. This improves the thermal conduction in composites over the pure matrix. For small particles embedded in the polymer matrix, interfaces also play an important role for controlling the thermal transport properties, particularly thermal conductivity. This is because of the involvement of increasing interface density which is responsible for the increased phonon-interface scattering and inturn for the decrease of thermal conductivity. However, for small concentration of the CdS or ZnS nanoparticles the effective thermal conductivity is more influenced by the higher thermal conductivity material (CdS 42.7W/mK [8], ZnS 17.4 W/mK [9]) and not by the presence of interfaces. It has also been observed from figure that value of thermal conductivity of the CdS (or ZnS)- polymer composite having CdS (or ZnS) nano-particle concentration of 8 wt. percent is lower than the nanocomposite having 6 wt. percent of CdS (or ZnS) nano-particle in the entire range of temperature. It is interesting to note that the thermal conductivity of the nanocomposites containing 8 wt% of CdS (ZnS) into polymer have got the thermal conductivity even less than the thermal conductivity of pure polymer for all the temperatures in the study. This could be explained on the basis of the existence of excess free volume over the pure polymer obtained due to strong agglomeration of CdS and ZnS nanoparticles into the polystyrene polymer. This phenomenon is also explained [10] by very low efficiency of heat transfer due to interfacial thermal resistance between particles and matrix, so that the higher thermal conductivity of the filler cannot be taken into advantage and the composite behaves like a hollow material, thus reducing its conductivity compared to the dense reference matrix.



Fig. 6. Temperature dependence of thermal conductivity for CdS/PS nano-composites



Fig. 7. Temperature dependence of thermal conductivity for ZnS/PS nano-composites



Fig. 8. Temperature dependence of thermal conductivity for CdS/PVC nano-composites

#### 3. Dynamic Mechanical Analyzer (DMA)

Dynamic Mechanical Analyser (DMA) is widely used to characterize a material's mechanical properties, such as modulus (elasticity) and viscosity (damping) as a function of time, temperature, frequency, stress or combinations of these parameters. It is most useful for observing the viscoelastic nature of polymers. Two methods are currently used. One is the decay of free oscillations and the other is forced oscillation.

Free oscillation techniques involve applying a force to a sample and allowing it to oscillate after the force is removed. Forced oscillations involve the continued application of a force to the sample. An oscillating force is applied to a sample of material and the resulting displacement of the sample is measured. This method is the most commonly used one today.

### 3.1 Principle of DMA – Forced Non-resonance Technique

The forced non-resonance technique is one of the simpler dynamic mechanical methods to understand.

In this instrument, a force (stress) is applied to the sample through the motor. The stress is transmitted through the drive shaft onto the sample, which is mounted in a clamping mechanism. As the sample deforms, the amount of displacement is measured by the Linear Variable Differential Transformer (LVDT) positional sensor. This LVDT mounted on the driven arm measures the sample response, strain and frequency as a function of stress and provides feedback to the motor as shown in Fig. 9. Therefore, the strain is calculated from the observed displacement. The force (or stress) is applied sinusoidally with a defined frequency. A DMA is often referred to as a DMTA (Dynamic Mechanical Thermal Analyzer) as during the measurement, the temperature of the sample is defined and can be changed. Sample is mounted inside the environmental chamber i.e. furnace. The test specimen is clamped between the movable and stationary fixtures and distance between the fixtures is adjustable. The magnitude of the applied stress and the resultant strain are used to calculate the stiffness of the material under stress. The phase lag between the two is used to determine the damping factor ( $\tan \delta$ ).



### Fig. 9. Pictorial display of DMA component

### 3.2 Theory and Instrumentation of DMA

Dynamic mechanical analysis (DMA) yields information about the mechanical properties of a

specimen placed in minor, usually sinusoidal, oscillation as a function of time and temperature by subjecting it to a small, usually sinusoidal, oscillating force. The sample can be mounted in DMA in a number of ways depending on the characteristics of the sample. The six common geometries are single cantilever bending, dual cantilever bending, 3 point bending, tension, compression and shear.

The applied mechanical load, that is, stress, elicits a corresponding strain (deformation) whose amplitude and phase shift can be determined, Fig. 10. The sample is subjected to pre-selected force amplitude and the resulting deformation is measured. The oscillatory strain wave results in oscillatory stress response with a phase lag ( $\delta$ ), which is a measure of viscous contribution. The phase angle or the loss angle, generally denoted as  $\delta$ , gives the amount by which the strain lags behind the resultant of the stress. The more delayed the response, the more viscous is the material while less delayed response are characteristic of more elastic material [11]. For perfectly elastic materials like steel the phase angle is zero ( $\delta = 0^{\circ}$ ) and for purely viscous materials such as a liquid, the phase angle is 90°. Viscoelastic materials fall in between these two extremes i.e.  $0^{\circ} <$  $\delta < 90^{\circ}$ . Most polymers exhibit this behaviour and have an elastic and viscous component.



Fig. 10. Sinusoidal oscillation and response of a material

When the sample is subjected to sinusoidal stress, it is deformed sinusoidally within linear viscoelastic region. The stress applied to the material at any time t is

$$\sigma = \sigma_0 \sin \omega t \tag{7}$$

where  $\sigma$  is stress at any time,  $\sigma_0$  is maximum stress at the peak of sine wave,  $\omega$  is frequency of oscillation and t is time.

The rate of variation of stress with respect to time is given by

$$d\sigma/dt = \omega \sigma_0 \cos \omega t \tag{8}$$

The resulting strain wave depends upon the extent of elastic and viscous behaviour exhibited by the material. Therefore, strain at any time t is

$$\epsilon(t) = \frac{\sigma}{E} = \frac{\sigma_0 \sin \omega t}{E}$$

Therefore,  $\varepsilon(t) = \varepsilon_0 \sin \omega t$ 

where E is the modulus and  $\varepsilon_0$  is the strain at maximum value of stress.

The phase lag between the applied stress and resultant strain is an angle  $\delta = \pi/2$  for viscous material.

i.e. 
$$\varepsilon$$
 (t) =  $\varepsilon_0 \sin (\omega t + \delta)$ 

We can rewrite as

$$\varepsilon (t) = \varepsilon_0 [\sin \omega t \cos \delta + \cos \omega t \sin \delta] \qquad (9)$$

Here,  $\varepsilon' = \varepsilon_0 \sin \delta$  and  $\varepsilon'' = \varepsilon_0 \cos \delta$ 

Therefore, the complex strain of material is as follows

$$\epsilon^* = \epsilon' + i\epsilon''$$

and complex modulus of a material,  $E^* = E' + iE''$ 

Hence, 
$$E' = \sigma_o / \epsilon' = \sigma_o / \epsilon_o \sin \delta$$
 (10)

and 
$$E'' = \sigma_o / \varepsilon'' = \sigma_o / \varepsilon_o \cos \delta$$
 (11)

By comparing Eq. (10) and (11), we have

$$E'' = \frac{E' \varepsilon_0 \sin \delta}{\varepsilon_0 \cos \delta}$$
  
i.e.  $\frac{E''}{E'} = \operatorname{Tan} \delta$ 

where  $\tan \delta$  is the damping factor, which is indicator of how efficiently the material loses energy in molecular arrangements and internal friction.

Dynamic mechanical testers apply a periodic stress or strain to a sample and measure the resulting strain or stress response. The stress which is in phase with the applied strain, is used to determine the elastic or storage modulus (E'), which is an indicator of elastic behaviour and reveals the ability of the material to store elastic energy associated with recoverable elastic deformation. The stress which is out of phase with the applied strain is used to calculate the viscous or loss modulus (E"). This modulus is an indicator of the ability of the material to absorb energy that is not released with the recoverable elastic transformation. This energy is used to increase segmental molecular vibration or to translate chain positions [12]. The loss tangent (tan  $\delta$ ) or mechanical damping is the phase angle between the dynamic strain and stress in the oscillating experiment. It is dimensionless and is given by the ratio of the viscous modulus to the elastic modulus [13].

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### 3.3 Measurement of Thermo-mechanical Properties of Different Polymer Nanocomposites

The study of mechanical properties of CdS/PMMA, ZnS/PMMA CdS/PS, ZnS/PS, CdS/PVC and ZnS/PVC nanocomposites in the form of films (thickness  $\approx 0.1 \text{ mm}$ ) such as loss factor, tan  $\delta$ , storage modulus, stress-strain relation, tensile strength, elongation at break etc. have been investigated using TRITEC 2000 Dynamic MechanicalAnalyzer (DMA).

The storage modulii for CdS /PMMA and ZnS/ PMMA nano-composites with different wt. % of CdS and ZnS have been recorded from room temperature to 140 °C as shown in Figs. 11 and 12 respectively [14-16]. It was observed that the storage modulii decrease sharply with the increase of temperature and attain a constant value after a certain value of temperature for both the nanocomposites. This behaviour of storage modulus is explained on the basis of mobility of molecular segments in polymer. In the lower temperature range, the oscillations of the molecules about the mean position are small due to their low kinetic energy. The modulus shows the maximum value at room temperature. When temperature is increased, the kinetic energy of molecules increases which increases the mobility of molecular segments (oscillation of molecules in polymer), resulting in an increase in the free volume between the molecular segments [17], thereby reducing the storage modulus. It is also observed that storage modulii for both CdS/PMMA and ZnS/PMMA nanocomposites increase with the increase of nanoparticle concentration upto 6 wt. %. However, storage modulus decreases at higher filler concentration (8 wt. %). The increase in storage modulii for CdS/PMMA and ZnS/PMMA nano-composites

reveal the excellent dispersion of CdS and ZnS nanoparticles in PMMA matrix, which is also confirmed from TEM measurement and a correspondingly large amount of interfacial area with altered polymer chain mobility throughout the composite. The decreasing values of storage modulii with higher filler concentration (8 wt %) indicate that nano-fillers agglomerate in polymer matrix, which is further confirmed from the TEM images. This suggests the lower dispersion ability of CdS and ZnS nanoparticles at higher wt. percentage.



Fig. 11. Variation of storage modulus of CdS/ PMMA nano-composites with temperature.



Fig. 12. Variation of storage modulus of ZnS/ PMMA nano-composites with temperature.

The variations of tan  $\delta$  with temperature for all CdS/PMMA and ZnS/PMMA nano-composites have been measured from room temperature to 140 °C [14-16]. It is observed that the value of tan  $\delta$  increases with an increase in temperature and reaches a maximum value at a particular temperature. Beyond this temperature, tan  $\delta$ decreases with the increase in temperature. This particular temperature at which the tan  $\delta$  shows its maximum value is known as glass transition temperature  $(T_g)$  or alpha transition temperature.  $T_g$ represents the temperature at which the polymer transforms from hard glassy state to soft rubbery state. It is also observed that for both the nanocomposites there is a slight shift in the tan  $\delta$ peak toward higher temperature as compared to pure polymer. It is noticed that the addition of more nano fillers resulted in a decrease in the magnitude of the tan  $\delta$  peak and an increase in its peak width. The height depression in the tan  $\delta$  peak is due to the reduction in the amount of mobile polymer chains during the glass transition [18] and also because of the good adhesion between the polymer and nanoparticles [19, 20]. Composition dependence of glass transition temperature is similar to that as obtained for storage modulus.

Similar behavior has been observed for the storage modulus and tan  $\delta$  of CdS/PS, ZnS/PS, CdS/ PVC and ZnS/PVC nanocomposites with temprature [21, 22]. However, storage modulus and glass transition temperature increase with the increase of nanoparticles concentration upto 4 wt. % for PS based nanocomposites and upto 2 wt. % for PVC based nanocomposites. Beyond these wt. %, storage modulus and glass transition temperature decrease. The increase in storage modulii and glass transition temperature for CdS/PS (or PVC) and ZnS/PS (or PVC) nanocomposites at low filler content is due to the excellent dispersion of CdS and ZnS nanoparticles in PS (or PVC) matrix, which is also confirmed from TEM measurement and a correspondingly large amount of interfacial area with altered polymer chain mobility throughout the composite. The decreasing values of storage modulii and glass transition temperature with higher filler concentration (above 4 wt. % of CdS and ZnS in PS and above 2 wt. % of CdS and ZnS in PVC) indicate that nano-fillers agglomerate in polymer matrix, which is further confirmed from the TEM images. This suggests the lower dispersion ability of CdS and ZnS nanoparticles at higher wt. %.

The apparent activation energy of the glass transition region (energy required for segmental motion of chains to reach glass transition region) for ZnS/PMMA, CdS/PVC and ZnS/PVC nanocomposites assuming non-Arrhenius behavior of viscosity, which is determined using storage and loss modulus, has been obtained through Vogel-Fulcher-Tammann (VFT) equation as shown in Figs. 13 and 14 respectively [16,22]. It is observed that apparent activation energy increases with the increase of nanoparticles up to 6 wt. % in PMMA matrix and upto 2 wt. % in PVC matrix. Beyond this wt. % of nanoparticles, activation energy decreases. The variation of activation energy as a function of nanoparticle content can be explained on the basis of the variation of their corresponding glass transition temperature  $(T_{\sigma})$ . As mentioned above, the glass transition temperature increases as we increase the nanoparticle content, but a higher value is observed for 6 wt. percent of nanoparticles in PMMA and for 2 wt. percent of nanoparticles in PVC. This higher value of T<sub>g</sub> is attributed to the rigid structure of polymer for this particular content of nanoparticle fillers. For such a rigid structure it is inferred that segmental motions are less and the energy required for such motion is higher as compared to other contents for the occurrence of glass transformation. The higher value of  $T_{\sigma}$  also indicates that the sample

is more thermally stable against rubbery behavior and then it can be concluded that thermal stability of sample increases upto 6 wt. percent of ZnS nanoparticles into PMMA matrix and 2 wt. percent of CdS and ZnS nanoparticles into PVC matrix and decreases beyond this wt. % of nanoparticles.



### Fig. 13. Composition dependence of glass transition of apparent activation energy of ZnS/PMMA nanocomposites



Fig. 14. Composition dependence of glass transition activation energy of CdS/ PVC and ZnS/PVC nanocomposites.

The stress-strain behavior of CdS/PMMA, ZnS/PMMA, CdS/PS, ZnS/PS, CdS/PVC and ZnS/PVC nanocomposites with different weight per cent of CdS and ZnS nanoparticles have also been studied at room as well as at elevated temperatures [3, 15, 21, 23-25]. Representative curves for stressstrain behavior of CdS/PS nanocomposites at room temperature and at different temperatures have been shown in Figs. 15 and 16 respectively. It has been observed that stress-strain curves show two characteristic regions and one phase transition. The first region is characterized by an initial linear increase, which gives the value of Young's modulus. The second one is characterized by the increase in the strain with very slow increase of the stress, which is specific for plastic deformation. The stress-strain relation gives the information about the Young's modulus (slope at the origin), yield point, tensile strength, fracture energy (the total area under the stress-strain curve) and recovery behavior of polymer films. It is observed that CdS/PMMA, ZnS/PMMA, CdS/PS and ZnS/PS nanocomposites show no yield point and no break point at room temperature. This is due to the fact that in the given experiment the applied force of 10N is not sufficient (the limit of applied force used in the experiment is 10N) to produce any yield and break point. Hence, it is not possible to obtain the value of fracture energy at room temperature.

Temperature dependence of stress-strain curves show that initial slope of curve (Young's modulus) and tensile strength are maximum for all composites at room temperature. Young's modulus and tensile strength decrease with the increase in temperature. This behavior of stress-strain curves can be explained on the basis of molecular motion of polymer chains. At low temperature, the structure is rigid and compact therefore the molecular motion in polymer is small due to the low kinetic energy of molecules, which ultimately leads to high Young modulus and tensile strength. As the temperature is increased, the kinetic energy of molecules increases, which further increases the molecular motion resulting in an increase in the distance between molecular segments, thereby decreasing the abovementioned properties. On further increasing the temperature i.e. at temperature  $(70^{\circ}C \& 90^{\circ}C)$  in the vicinity of glass transition temperature, the molecular motion is fast enough for viscous flow, the structure of samples becomes soft and rubbery. This consequently decreases the Young's modulus and tensile strength to a great extent and very low values of Young's modulus and tensile strength are obtained. It can be seen that the mechanical properties such as Young's modulus, tensile strength and fracture energy increase with the increase of CdS and ZnS nanoparticles upto 6 wt. % in PMMA, upto 4 wt. % in PS and upto 2wt. % in PVC. Beyond this wt. % of nanoparticles, the mechanical properties decrease. The results obtained from this study are explained on the basis of interaction between nanoparticles and polymer [26,27]. The interaction between nanoparticles and polymer is identified through C-S (630 cm<sup>-1</sup>) bonding which is given by FTIR spectra. It is also observed that initial slope of curve (Young's modulus) and tensile strength are maximum for all composites at room temperature. Young's modulus and tensile strength decrease with the increase in temperature. This behavior of stress-strain curves can be explained on the basis of molecular motion of polymer chains.







Fig. 16. Stress-strain behavior for CdS/PS at different temperatures

#### 4. Differential Scanning Calorimetry (DSC)

Differential Scanning Calorimetry (DSC) is commonly used thermal analysis technique which provides fast and convenient analysis of glass characteristics such as  $T_g$  and temperature of phase changes, for instance devitrification and melting. DSC allows accurate measurement of enthalpy change during heating at controlled heating rate. A DSC measures the energy changes that occur as a sample is heated, cooled or held isothermally, together with the temperature at which these changes occur.

The basic principle underpinning DSC is that a sample is subjected to a heat signal and the response measured in terms of the energy and temperature of the thermal events that take place over the temperature range or time interval under study.

Based on mechanism of operation DSC can be classified into two types.

- Power Compensated DSC
- Heat flux DSC

### 4.1 Properties that can be Studied using DSC

- 1. Kinetics of Phase transformations
- 2. Thermal Stability and Thermodynamics
- 3. Structural Relaxation

DSC has found use in many wide ranging applications including polymers and plastics, foods and pharmaceuticals, glasses and ceramics, proteins and life science materials; in fact virtually any material, allowing the analyst to quickly measure the basic properties of the material.

## 4.2 Activation Energy and Thermal Stability of CdS/PMMA Nanocomposite

An effort has also been made to study the thermal stability of CdS/PMMA nanocomposites through the differential scanning calorimetry (DSC) measurements [28]. Fig. 17 gives the DSC thermogram for CdS/PMMA nano-composites with different weight percent of CdS nanoparticles at 25 K min<sup>-1</sup> heating rate. Similar DSC thermograms have been obtained for each composite at different heating rates (5, 10, 15 and 20 K min<sup>-1</sup>). The peak glass transition temperatures have been determined using the DSC thermograms. It is found that the glass transition temperature increases with the increase of CdS content up to 6 wt. percent and then decreases for higher wt. percent (8 wt. percent). It is explained on the basis of molecular motion of PMMA, which is restricted on addition of CdS into PMMA. The activation energy of glass transition in the case of nanocomposites of different weight percent of CdS has been determined. Variation of activation energy with CdS nanoparticle concentration has also been theoretically predicted by using an empirical relation [28] as shown in Fig. 18.

Thermal stability of so prepared nanocomposites has been explained with the help of activation energy in the glassy region. CdS/PMMA nanocomposite with 6 wt. percent of CdS nanoparticles shows the highest thermal stability over the composites with other compositions.



Fig. 17. DSC thermograms at 25 K/min heating rate for CdS/PMMA nanocomposites.



Fig. 18. Variation of activation energy as a function of CdS wt. percent

### 5. Conclusions

Some thermal characterization techniques such as transient plane source method, dynamic mechanical analysis and differential scanning calorimetry have been discussed briefly. These techniques are extremely useful in material characterization from the view point of their thermal, thermo-mechanical and their thermal stability at room as well as at elevated temperature. The thermal conductivity, mechanical properties such as storage modulus, tensile strength, toughness, tan  $\delta$  etc., and activation energy of some CdS and ZnS based polymer nanocomposites such as CdS/PMMA, ZnS/PMMA, CdS/PS, ZnS/PS, CdS/PVC and ZnS/PVC with their temperature and composition dependence have been studied. The results indicate that an increment is observed for both thermal conductivity and mechanical properties with the increase of CdS (or ZnS) content in PMMA up to 6 wt. percent whereas for PS similar behavior is obtained upto 4 wt. percent of nanoparticles and for PVC up to 2 wt. percent of nanoparticles. Beyond this percent both the properties decrease. These results are explained on the basis of particles-polymer interaction. Temperature dependence of thermal and mechanical properties indicates that the thermal conductivity increases with the increase of temperature (up to glass transition temperature and then become constant) whereas mechanical properties decrease with the increase of temperature and then become constant after a certain temperature. The variation of mechanical properties and thermal conductivity of these nanocomposites with temperature helps us in deciding about the range of temperature in which material could be used for a particular application without any change in its behavior.

### 6. Acknowledgement

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## N. S. SAXENA

### N. S. SAXENA

**N.S. Saxena** received a M.Sc. (1969) and a Ph.D. (1975) in Physics from Department of Physics, University of Rajasthan, Jaipur, India. He is retired Professor of Physics from the University of Rajasthan and currently working as Emeritus Fellow UGC in the same University. He was postdoctoral fellow of International Programme in Physics, Uppsala, Sweden (1985-86). He has collaborated in the design criteria of TPS technique (now called Hot- Disk 2500) for the measurement of thermal transport properties of solids with Prof. S.E. Gustafsson, Chalmers University of Technology, Gothenburg.

He has supervised more than 35 students for their Ph.D. degree in Physics and published more than 330 papers in international and national journals of repute. He has 40 yrs research experience in the field of condensed matter physics.

Prof. Saxena has delivered more than 25 Invited Talks and chaired the sessions at national and international conferences and workshops. He was member of the editorial board of Indian Journal of Pure and Applied Physics for the period 2002-2007. He has edited proceeding of International Conference on the Physics of Disordered Materials published by NISCOM, New Delhi, 1997 and National Conference of Thermo-physical Properties (NCTP-05) published by American Institute of Physics, USA, 2010. He is the author of more than 20 books of undergraduate level. He is the life member of more than 6 scientific societies. At present he is the president of Thermo-physical Society of India (TPSI).


# D. PATIDAR

### D. PATIDAR

**D. Patidar** received a M.Sc. in Physics from Maharshi Dayanand Saraswati *University*, Ajmer, India in 2003 and a Ph.D in Material Science from University of Rajasthan, Jaipur, India in 2007. He is currently working as Research Scientist DST at the Department of Physics, University of Rajasthan, Jaipur, India.

He has published more than 40 papers in the National and International journal of repute. His research interest includes synthesis of chalcogenide nanomaterials, organic/inorganic nanocomposite, inorganic/ inorganic heterojunctions, metal/semiconductor junctions and their structural, optical, electrical and mechanical properties.

Dr. Patidar Received JRF and SRF for Defence Research & Development Organization (*DRDO*), Govt. of India and RA from Council of Scientific and Industrial Research (CSIR), Govt. of India. He also received DST Fast Track Young Scientist award from DST, Govt. of India. He is the life member of Thermo-Physical Society of India (TPSI).

### REPORT ON Thermans 2013

The Nineteenth National Symposium and Workshop on Thermal Analysis (THERMANS-2013) and workshop were held at TSH & HBNI, Bhabha Atomic Research Centre during December 19-23, 2013.

There was overwhelming response to the symposium a significant percentage of student and research scholar participants. In all there were 240 registered participants from academic and research institutions with a significant percentage of student and research scholar participants.

Smt. Jhimli Paul Guin welcomed the participants of this symposium. Dr. Shyamala Bharadwaj, Convener of the Symposium gave an account of how the Indian Thermal Analysis Society has been arranging the biennial symposia without a break since 1977. She pointed out that this was possible because of the financial support from BRNS and the enthusiasm of local organizers from various universities and other national laboratories.

The symposium was inaugurated by Dr. K. L. Ramakumar Director, Radiochemistry & Isotope Group, BARC. Dr. B. N. Jagatap, Director Chemistry Group was guest of honour for the inaugural function. Dr D. Das, President, Indian Thermal Analysis Society ITAS) cited the active role played by thermal analysis techniques in characterization of materials for specific purposes. He also pointed out that thermal analysis will have a greater role to play in the coming years as the Department of Atomic Energy is taking on the challenging tasks pertaining to PFBR, AHWR, CHTR fuel development, materials problems for ADS, SOFC, thermo-chemical water splitting for production of hydrogen using nuclear heat etc.



Inaugural function of THERMANS 2013. From right to left: Dr. K. L. Ramakumar (Director, Radiochemistry and Isotopes Group, BARC), Dr. Shyamala Bharadwaj (Convener, THERMANS 2013), Dr. B. N. Jagatap (Director, Chemistry Group, BARC), Dr. D. Das (President, ITAS) and Dr. Y. K. Bhardwaj (Secretary, THERMANS). In his thought provoking inaugural address, Dr. K. L. Ramakumar emphasized how thermal analysis techniques are being increasingly looked upon as a highly reliable tool for material characterization particularly for nuclear fuels. He mentioned that material scientists effectively make use of Thermogravimetry, as hyphenated tool in conjunction with Mass Spectrometry (TG-MS), with Differential Scanning Calorimetry (TG-DSC), with FT-Infrared Spectroscopy (TG-FTIR) etc. for understanding the basic thermal phenomena and the material properties. He also pointed out that the best way to enthuse the young researchers is to give challenging assignments to them. The proceedings of the symposium containing the lectures from experts were released by Dr. K. L. Ramakumar and were distributed to the delegates. A Souvenir was brought out by the Indian Thermal Analysis Society on this occasion and was released by Dr. B. N. Jagatap. For the first time in this series of symposia pen drives (PDs) containing both the symposium proceedings and workshop lectures were brought out. Dr. D. Das released these PDs and they were also distributed to the delegates.

Dr. S. C. Parida, Secretary, ITAS, announced the awards instituted by the Indian Thermal Analysis Society. The awards were presented by Dr. K. L. Ramakumar, Dr. B. N. Jagatap, Dr. D. Das and the sponsors of the awards. SETARAM-ITAS Calorimetry Excellence Award was conferred on Dr. V. Venugopal. NETZSCH-ITAS Award 2013 was conferred on Dr. (Mrs.) Bina N. Wani, of Chemistry Division BARC, Mumbai for her outstanding contributions to field of thermal analysis. The TA Instruments-ITAS Young Scientist Award 2013 was conferred on Shri Bhaskar Paul of Materials Processing Division, BARC. Dr. M. D. Karkhanavala Memorial Essay Contest 2013 was won by Shri Subhasis Pati, JRF, BARC. Dr. Gurdip Singh Award for Best Thesis in Thermal Analysis 2013 was given to Dr. Puja Paul of Jadavpur University, Kolkata.

Dr. B. N. Jagatap, inaugurated the exhibition where 12 vendors including two from abroad displayed their products.

There were 08 technical sessions, 01 instrumentation session and 13 invited lectures. Three of the invited lectures were by experts from abroad. More than 120 research papers were presented at the symposium in oral and poster sessions.

ITAS awarded cash and merit certificates for best papers presented in both oral and poster sessions. In order to encourage the young researchers in the field of thermal analysis, the oral presentations were restricted to research scholars below the age of 35.

The THERMANS 2013 workshop was inaugurated by Dr. B. N. Jagatap, Director Chemistry Group. Workshop proceedings were also released by Dr. Jagatap during inaugural session. In the workshop, there were 35 research scholars and student participants. There were 10 invited lectures by eminent scientists on various aspects of thermal analysis. Various experimental techniques such as high temperature XRD, Solid state electrolytes, phase transformation kinetics, calorimetry etc. were dealt with M/s V. N. Engineering, Mumbai displayed their indigenously developed DTA instrument during the workshop. The workshop participants got hands-on experience on the instrument. A lot of interest was shown in the indigenously developed instrument by the participants because of the reliable data output and low cost.

### BOOK Review



The book entitled "Kinetics of Heterogeneous Solid State Processes" authored by Dr. Pritam Deb is published in 2014 as Springer Briefs in materials.

Study of kinetics of various phenomena has proved to be extremely challenging task among researchers and scientists in different fields like Physics, Chemistry, Materials Science and even life sciences. A qualitative interpretation of various processes is not sufficient to understand them and one needs to quantify them in terms of process parameters like activation energy, frequency factor, order of reaction etc. In this direction, lots of efforts have been made by quite large number of researchers putting forward different equations and deriving these process parameters applying some assumptions or the other. These assumptions, in turn, have led to approximations. Owing to this, uniqueness and reproducibility of the evaluated quantities describing different reactions including phase transformation, solid state precipitation, crystallization, glass transition, oxidation and decomposition have always been in question. In light of this, this book is a novel effort to investigate the fundamental concepts of kinetics of various processes in general and that of heterogeneous processes in solid state in particular.

The book consists of five chapters devoted to different aspects of kinetics followed by summary of the entire work. Chapter-1 introduces the fundamental concepts of kinetics. On these nuclei of concepts, subject of kinetics grows in subsequent chapters 3 to 5. Chapter-2 discusses material development and the involved process with particular reference to nano-sized particles ranging in mean diameter from 1 to 100 nm. Chapter-3 provides details of non-isothermal method of kinetic analysis including identification of the kinetic law and evaluation of kinetic energy. Kinetic equation under rising temperature has been derived without any apriori knowledge or assumption of mechanism. For single heating rate, the equation appears to be of the form of the

one given by Coats and Redfern. The form of the model for the function  $f(\alpha)$  seems to be different for evaluation of  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> given in chapter-4 on kinetics of a solid state process. Chapter-5 seems to be the heart of the present book with a detailed description of the heterogeneous solid state process and the kinetics involved in it. In this chapter, a method has been given for the deconvolution of a DSC plot in order to identify the intermediate processes. The deconvolution was preceded by plotting d<sup>2</sup>H/dT<sup>2</sup> as a function of T with H being the heat flow.

Based on the methods given in the present book, it is expected that the material contained in this will pave the way to separate overlapping peaks in a complex reaction. Analysis of the results following the prescription offered by the author will lead to deeper insights into the kinetics of heterogeneous processes and will prove to be a milestone for many young minds.

Prof Arun Pratap

Tuesday, 12<sup>th</sup> August, 2014 International Youth Day

### FORTHCOMING Events

- TAC 2015. 50<sup>th</sup> Anniversary Conference of the RSC Thermal Methods Group at Churchill College, Cambridge to be held during 30th March to 1st April 2015. This 3 day event in the historic University City of Cambridge offers a unique opportunity for attendees to hear about the past, present and future of Thermal Analysis and calorimetry. Last date of submission of abstract (up to 300 words) for paper or poster presentation is 30th September 2014. Contact. ian.priestley@syngenta.com.
- 2. The 2015 Users Meeting and Symposium, to be held at *San Antonio, Texas during February 15-18* 2015 provides a stimulating venue for anyone involved in Thermal Analysis, Rheology, or Microcalorimetry to learn about and share in the latest practices, techniques, and advances in these analytical techniques. This meeting is specifically intended for all scientists, chemists and lab managers who use TA Instruments or competitive systems and want to better understand the measurement technology and industry-specific applications.
- 3. IFPAC—International Forum on Process Analytical Chemistry (IFPAC) 2015, during 25 28 January 2015 at Arlington, US. Weblink. http://www.ifpac.com/

The three day forum will focus on the latest developments in Process Analytical Technology...emerging techniques, new applications, instrumentation, software, standards, and a look into the future. Process Analytical Technology is one of the most exciting and important advanced technology areas meeting both the current challenges, as well as the future needs of industry.

## SATAC-2014

Indian School of Mines (ISM), Dhanbad (Jharkhand) December 15-17, 2014

'Thermal analysis' has emerged as one of the most versatile techniques, having applications in almost all branches of science. The Indian Council of Chemists (ICC) organized SATAC-2010, the first such symposium on Applications of Thermal Analysis and Calorimetry in India. It was during the 29th ICC at Chandigarh in December, 2010 and, was a grand success. A special Volume was brought out (Vol 107, No 1, January 2012) by Journal of Thermal Analysis and Calorimetry to commemorate the event of "29<sup>th</sup> ICC-SATAC 2010" (www.springeronline.com/jtac/10973). The next year, the Association of Chemistry Teachers organised National Convention of Chemistry Teachers (NCCT) in 2011 and during that event too, a SATAC was held (SATAC-2011) and JTAC published an issue devoted to SATAC-2011. These issues were besides the Special JTAC issues that are published devoted to THERMANS every alternate year. These events definitely contribute to the advancement of Thermal Analysis.

This year too, the Indian Council of Chemists (ICC) has decided to devote one day (December 16, 2014) for an International SYMPOSIUM ON APPLICATIONS OF THERMAL ANALYSIS AND CALORIMETRY: WORKSHOPAND EXHIBITION (named, SATAC-2014) during its 3-day Annual Conference which is being held at Indian School of Mines (ISM), Dhanbad (Jharkhand) [http://www.ismdhanbad.ac.in/] this year (15-17 December 2014). Areas covered shall include all branches of applications of THERMAL ANALYSIS AND CALORIMETRY. Nearly 300 chemistry researchers from all over India are expected. It will be a unique platform for bringing academia, R&D, industry and manufacturers of thermo analytical instruments, together. Papers have been invited for presentation at the Symposium in oral/poster sessions. Interested persons are submitting their abstracts (250 words) to profrkverma@gmail.com. The last date is November 25, 2014.

ICTAC



### INTERNATIONAL CONFEDERATION FOR THERMAL ANALYSIS AND CALORIMETRY

### NATAS Welcomes ICTAC 2016

Please join us in Orlando, Florida August 11 – 21, 2016

At the Walt Disney Swan & Dolphin Hotel & Conference Center

Upscale guestrooms, Inviting meeting space, Free shuttle service to parks, 17 on-site restaurants, exclusive Disney options

An exceptional locale for the union between science & imagination



The next ICTAC, 16<sup>th</sup> International Thermal Congress, ICTAC-2016 is going to be organised at Orlando, USA during August 14-19, 2016. The details were presented by the Conference Co Chairman, Bob Howell during the 50<sup>th</sup> meeting of ICTAC Executice Committee, on behalf of the hosts, NATAS, during the European Symposium, 11<sup>th</sup> ESTAC held at Helsinki, Finland

 Prof Ranjit K Verma Secretary, ICTAC The venue shall be the famous Disneyland. The proposed Sessions shall be:

Sessions	Co-Chairs
High Temperature Thermal Analysis	Brain Grady
Composites, Nano-composites	Prashanth Badrinarayan
Polymer Stability, Degradation & Flammability	Mark Beach
Rheology & Viscoelasticity	Leela Rakesh
Thermal Transport & Electrical Properties	Rob Campbell
Thin Film & Nanoconfinement	Connie Roth
Environmental Sustainability & Green Chemistry	Wei-Ping Pan
Kinetics and Catalysts	Sergey Vyazovkin
Pharmaceuticals	Wenwen Huang
Biomaterials, Biopolymers	Patrick Smith
Energetic Materials & Thermal Hazards	Brandon Weeks
Computational Methods for Thermal & Rheological Properties	Rajesh Khare
Instrumentation & Methods	Stanislov Stoliarov
Fast Scanning Methods	Christoph Schick

### HONOURS AND BOUQUETS

#### ICTAC elects Prof. Verma as its Secretary

It is a moment of pride for ITAS that the International Confederation for Thermal Analysis and Calorimetry (ICTAC; www.ictac.org) has elected our Vice President, Professor Ranjit Kumar Verma to its Executive Committee as its Secretary. This assignment is for the 2012-16 term.

#### Dr. Shyamala Bharadwaj becomes Regional Editor of JTAC

It is a matter of honour that Dr. Shyamala Bharadwaj, Head, Fuel Cell Materials & Catalysis Section, Chemistry Division, BARC, who has been actively engaged in ITAS activities for several years has been appointed Regional Editor of Journal of Thermal Analysis & Calorimetry (JTAC), an International Journal of Thermal Science having Impact Factor of 2.206.

#### **Prof Verma (ITAS Vice President) appointed as Pro Vice Chancellor**

Prof R K Verma has been appointed as the Pro Vice Chancellor of Patna University (www.patnauniversity.ac.in) - the seventh oldest university of India, for a three year term through a Search Committee process.

#### IIM-KK Award for Prof. Arun Pratap

IIM-KK Award,2012 has been conferred on Prof. Arun Pratap, Professor of Condensed Matter Physics, The Maharaja Sayajirao University of Baroda and Guest Editor of this special issue of ITAS Bulletin on 'Kinetics' for his outstanding, selfless and meritorious contribution in Academics and R&D field in particular and metallurgical society in general in the state of Gujarat. This award was presented to him by Indian Institute of Metals (IIM), Baroda Chapter.

#### Copyright for Software for Dr. Pritam Deb

Dr. Pritam Deb, Tezpur (Central) University, who has contributed an article in this issue, has obtained copyright of a software named "Kinlac-Method for kinetic analysis of solid state processes from non-isothermal calorimetry" with M. Gogoi (no.SW 8075/2014).

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