

## Crystallization kinetics of $\text{Ni}_x\text{Ti}_{100-x}$ ( $x=35,40$ ) glasses before and after high energy heavy ion irradiation

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Non-isothermal crystallization process in amorphous alloys  $\text{Ni}_{35}\text{Ti}_{65}$  and  $\text{Ni}_{40}\text{Ti}_{60}$  before and after high-energy heavy ion irradiation with 150 MeV  $\text{Ni}^{+11}$  ions have been investigated using differential scanning calorimetry (DSC). The alloys have been irradiated with fluences varying between  $1 \times 10^{11}$  and  $1 \times 10^{13}$  ions/ $\text{cm}^2$ . DSC traces have been analyzed in terms of activation energy for crystallization, Avrami exponent dimensionality of growth by using four different models viz. Kissinger equation [J Res NBS, 57 (1956) 217], Ozawa equation [Bull Chem Soc Jpn, 35 (1956) 881], Matusita equation [J Mater Sci, 19 (1986) 291] and Gao and Wang equation [J Non-Cryst Solids, 87 (1980) 129]. No effect of heavy ion irradiation of above mentioned energy, on the crystallization kinetics has been found.

[Keywords: Amorphous alloys, Crystallization, Crystallization kinetics, Glasses]

### 1 Introduction

There is considerable interest in two-component metallic glasses, both as regards their basic physical properties and industrial applications. Technological applications of metallic glasses require that such materials should be thermally stable with time and temperature during use. Scientifically, the kinetics of crystallization is equally important in understanding the atomic processes involved in the formation of crystalline phases. The thermal stability of amorphous alloys can be defined as the resistance to crystallization and is given in terms of the on-set crystallization temperature.

Ion beam assisted techniques for the preparation and characterisation of metastable alloys are now quite widely used. Fast ions in matter lose their energy predominantly via two mechanisms; nuclear energy loss and electronic energy loss. For fast heavy ions the density of electronic excitations and ionization becomes so high that new and collective effects arise<sup>1,2</sup>.

Thus, investigations have been made to study the crystallization kinetics of  $\text{Ni}_x\text{Ti}_{100-x}$  ( $x=35,40$ ) amorphous

alloys before and after high energy heavy ion irradiation at different fluences. The obtained DSC traces have been analysed in terms of thermal stability, activation energy, dimensionality of growth and frequency factor. Finally, a comparative study has been made in order to see the effect of irradiation.

### 2 Experimental Details

Specimens, each of suitable size ( $1 \times 1 \text{ cm}^2$ ) were cut from amorphous ribbon of  $\text{Ni}_x\text{Ti}_{100-x}$  ( $x=35,40$ ), produced by the melt spinning technique. Specimens were cleaned ultrasonically prior to the experiment. The samples were irradiated with  $\text{Ni}^{+11}$  ion beam of 150 MeV energy at different fluences at Nuclear Science Centre (NSC), New Delhi (India). The amorphous nature of the samples was confirmed by X-ray diffraction before and after irradiation.

Differential scanning calorimetry (DSC) study was performed on Rigaku 8230 B attached with thermal analysis station (TAS) at five scanning rates; 5, 7, 10, 15 and 20  $\text{K min}^{-1}$ . The samples of masses of approximately

Table 1 — Onset-crystallization temperatures and peak crystallization temperatures obtained at different heating rates.

System	On-set crystallization temperature $T_c$ (K)					Peak crystallization temperature $T_p$ (K)				
	Heating rate (K/min)					Heating rate (K/min)				
	5	7	10	15	20	5	7	10	15	20
$\text{Ni}_{35}\text{Ti}_{65}$	690.1	693.3	699.1	702.1	706.2	719.4	723.1	725.4	730.0	735.0
$\text{Ni}_{46}\text{Ti}_{54}$	745.0	752.0	754.3	759.2	760.7	751.8	757.7	762.3	766.9	770.9

3 mg were continuously heated from room temperature to 973 K in dry nitrogen atmosphere. The instrument was calibrated prior to measurement by using high purity metal standard with known latent heat. The calibration and measurements of alloys were carried out using identical conditions for better accuracy.

### 3 Results and Discussion

Typical DSC traces of both glasses at the heating rates of 10K/min are shown in Fig.1

It is evident from the figure that both the glasses crystallize into a single stage. The characteristic temperatures ( $T_c$  and  $T_p$ ) both increase with the increase of Ni content. The values of  $T_c$  and  $T_p$  of both the glasses at all the heating rates employed here are reported in Table 1.

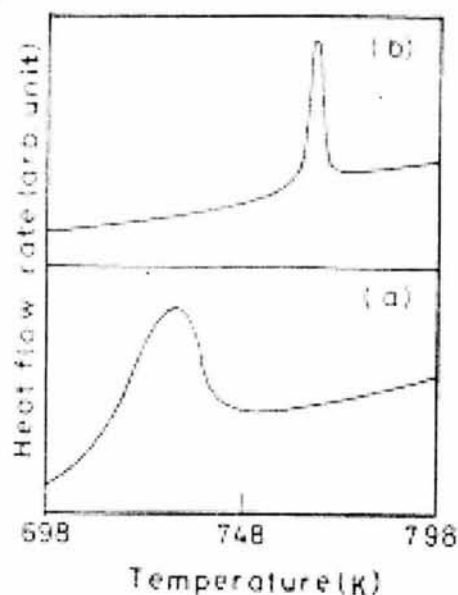


Fig.1 — DSC thermogram of  $\text{Ni}_x\text{-Ti}_{1-x}$  glasses at a heating rate of 10 K/min: (a)  $\text{Ni}_{35}\text{Ti}_{65}$  and (b)  $\text{Ni}_{46}\text{Ti}_{54}$

Further, DSC traces were analyzed to gain more insight of the kinetics of crystallization. The kinetic parameters have been evaluated using four theoretical models.

The activation energy for crystallization,  $E_c$  is determined using the Kissinger relation<sup>3</sup>:

$$\ln(\alpha/T_p^2) = E_c/RT_p + \text{constant} \quad \dots(1)$$

where  $\alpha$  is the heating rate and  $R$  is the gas constant. Fig. 2 shows the plot of  $\ln(\alpha/T_p^2)$  against  $1000/T_p$  for both the compositions. Both curves are linear. From the slopes of the straight lines, the activation energies are evaluated.

Further, the Ozawa equation<sup>4</sup>:

$$\ln(\alpha) = E_c/RT_c + \text{constant} \quad \dots(2)$$

is used to compute  $E_c$ . The plots of  $\ln(\alpha)$  against  $1000/T_c$  are straight lines as shown in Fig.3. Again the slopes

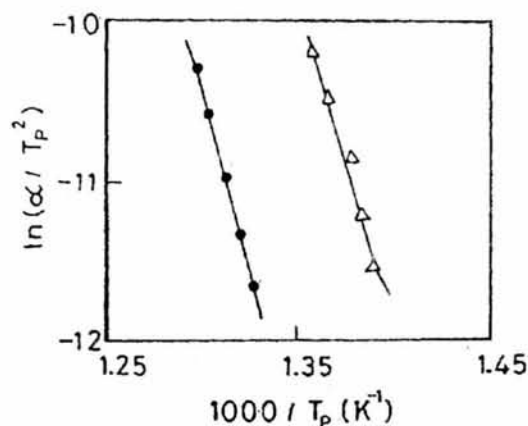


Fig. 2: — Kissinger plots for  $\text{Ni}_x\text{-Ti}_{1-x}$  glasses :  $\text{Ni}_{35}\text{Ti}_{65}$ ,  $\text{Ni}_{46}\text{Ti}_{54}$

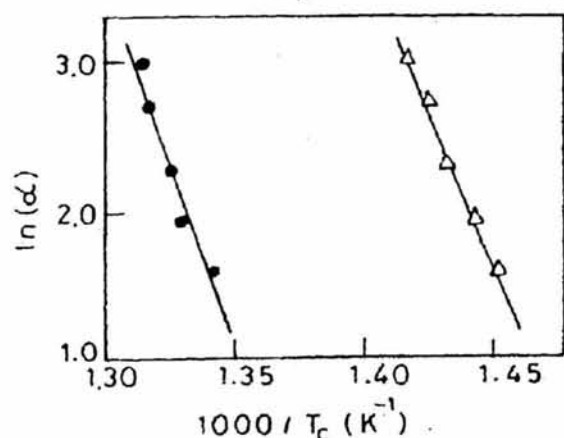
Fig 3 — Ozawa plots for  $\text{Ni}_x\text{-Ti}_{1-x}$  glasses:  $\text{Ni}_{35}\text{Ti}_{65}$ ,  $\text{Ni}_{40}\text{Ti}_{60}$ 

Table 2: Activation energy of crystallization calculated with different models

System	Activation energy (kJ/mole)			
	Kissinger Eq.	Ozawa Eq.	Matusita Eq.	Gao-Wang Eq.
$\text{Ni}_{35}\text{Ti}_{65}$	$348 \pm 5$	$345 \pm 7$	$377 \pm 10$	$355 \pm 8$
$\text{Ni}_{40}\text{Ti}_{60}$	$380 \pm 5$	$414 \pm 7$	$385 \pm 10$	$393 \pm 8$

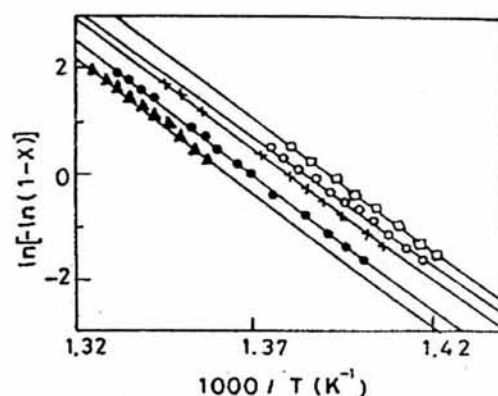
of the straight lines give the activation energies for both the compositions.

An attempt has also been made to calculate the activation energies of both the samples using the Matusita formulation<sup>5</sup>. Matusita's equation is given by:

$$\ln[-\ln(1-X)] = -n \ln(\alpha) - 1.052(mE_c/RT) + \text{constant} \quad \dots (3)$$

where  $X$  is the crystallized volume fraction and  $m$  and  $n$  are related to the dimensionality of growth. The plot between  $\ln[-\ln(1-X)]$  versus  $1000/T$  at constant heating rate,  $\alpha$  yields a straight line, the slope of which gives the activation energy for crystallization. The plots for both the glasses are displayed in Figs 4 and 5.

Further, Gao and Wang<sup>6</sup> have proposed a slightly different method to analyze DSC thermograms in terms of the activation energy ( $E_c$ ), the dimensionality ( $m$ ), the rate constant ( $K_p$ ), the frequency factor ( $K_o$ ), etc., during the crystallization process. The theory provides the

Fig. 4 — Matusita plots for  $\text{Ni}_{35}\text{Ti}_{65}$  glass at different heating rates: 5 K/min, 7 K/min, 10 K/min, 15 K/min and 20 K/min

relationship between the maximum crystallization rate and the peak crystallization temperature.

$$\ln(dX/dt)_p = -E_c/RT_p + \text{constant} \quad \dots (4)$$

where  $(dX/dt)_p$  is the rate of volume fraction crystallized at the peak of crystallization,  $T_p$ , which is proportional to the peak height. Fig 6. shows the plot of  $\ln(dX/dt)_p$  against  $1000/T_p$  for both the glasses. The activation energies at different compositions are determined from the slope of the straight lines.

The values of  $E_c$  for  $\text{Ni}_{35}\text{Ti}_{65}$  and  $\text{Ni}_{40}\text{Ti}_{60}$  glasses computed from above mentioned four models are reported in Table 2. It can be noted from the table that the value of  $E_c$  is higher for  $\text{Ni}_{35}\text{Ti}_{65}$ . The values calculated from different models differ slightly from each other. The difference in  $E_c$

values may be attributed to basic assumptions lying in different theories<sup>7</sup>. Further from the variation of  $\ln(1-X)$  with  $\ln\alpha$  at constant temperature the Avrami exponent ( $n$ ) has been calculated (Figure has not been shown). The Avrami exponent in  $\text{Ni}_{35}\text{Ti}_{65}$  is found to be 2 indicating one-dimensional growth, with surface crystallization. In contrast to  $\text{Ni}_{35}\text{Ti}_{65}$ , the value of Avrami exponent in  $\text{Ni}_{40}\text{Ti}_{60}$  glass (4) indicates three-dimensional growth along with bulk crystallization. The difference in the value of Avrami constant in both the glasses may also be assured from the DSC traces. It is clear from the Fig 1,

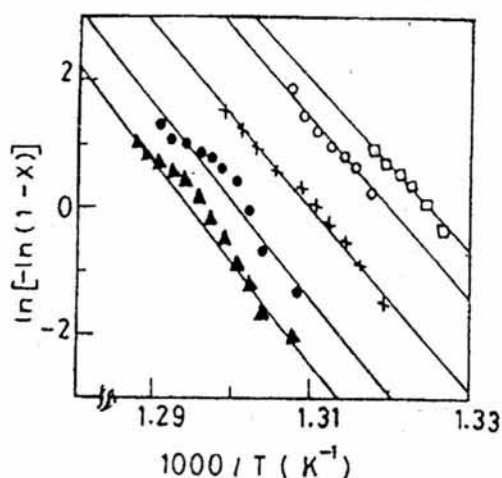


Fig. 5 — Matusita plots for  $\text{Ni}_{40}\text{Ti}_{60}$  glass at different heating rates: 5 K/min, oo 7 K/min, xx 10K/ min, 15 K/min. and 20 K/min

that the crystallization peak is relatively much sharper in  $\text{Ni}_{40}\text{Ti}_{60}$  glass as compared to that of  $\text{Ni}_{35}\text{Ti}_{65}$  glass.

To obtain more information about morphology of growth and Avrami exponent the following relations from Gao-Wang model have been used:

$$\begin{aligned} K &= K_0 \exp(-E_c/RT), \\ K_p &= a E_c/RT^2_p, \\ (dX/dt)_p &= 0.37 n K_p, \end{aligned} \quad \dots (5)$$

where  $n$  is Avrami exponent,  $K_p$  the reaction rate factor,  $K_0$  the frequency factor and other symbols have their usual meanings. The kinetic parameters, rate constant ( $K_p$ ), frequency factor ( $K_0$ ) together with  $n$  obtained from Gao-Wang relations are reported in Table 3. Table 3 also contains the values of Avrami exponent obtained from Matusita equation. The average value of Avrami exponent calculated from Gao-Wang equation. in both the glasses agree well with values obtained from Matusita equation.

#### 4 Crystallization Kinetics of Irradiated Specimens.

The DSC curves of both the glasses irradiated at different fluences at the heating rate of 20K/min are shown in Figs 7 and 8 respectively.

The DSC thermograms of virgin glasses are also plotted in the respective figures. No substantial change is observed in DSC thermograms after high energy irradiation.

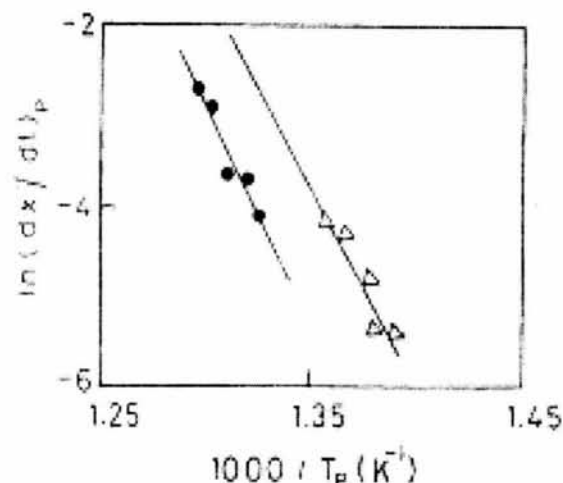


Fig.6 — Gao and Wang plots for  $\text{Ni}_x\text{-Ti}_{1-x}$  glasses:  $\text{Ni}_{35}\text{Ti}_{65}$ ,  $\text{Ni}_{40}\text{Ti}_{60}$

Generally the variation in  $T_c$  and  $T_p$  in the same system under identical experimental conditions is attributed to change in structure or formation of new phase in the glassy matrix during crystallization. The consequence of irradiation is only electronic excitations. Hence, no new phase is formed.

The activation energy of crystallization has been calculated using the peak-shift method of Kissinger. The activation energy of both the glasses comes out to be of the same order (324 and 396kJ/ mole respectively) as that of virgin one. The difference in  $E_c$  value is due to variation in  $T_p$  values in the fourth digit, and hence is not meaningful. The above results suggest that the high energy heavy ion irradiation produces defects in the

Table —3 The parameters of crystallization of Ni-Ti glasses

System	Heating rate(K/min)	$K_p$ (sec <sup>-1</sup> )	$K_0$ (sec <sup>-1</sup> )	$n$
$\text{Ni}_{35}\text{Ti}_{65}$	5	0.0097	$4.07 \times 10^{27}$	1.67
	7	0.0109	$4.03 \times 10^{27}$	1.14
	10	0.0155	$4.61 \times 10^{27}$	1.40
	15	0.0229	$3.79 \times 10^{27}$	1.58
	20	0.0302	$3.18 \times 10^{27}$	1.57
$\text{Ni}_{40}\text{Ti}_{60}$	5	0.0037	$1.53 \times 10^{20}$	4.21
	7	0.0057	$1.79 \times 10^{20}$	4.09
	10	0.0079	$1.97 \times 10^{20}$	4.37
	15	0.0112	$2.01 \times 10^{20}$	4.07
	20	0.0166	$2.19 \times 10^{20}$	4.95

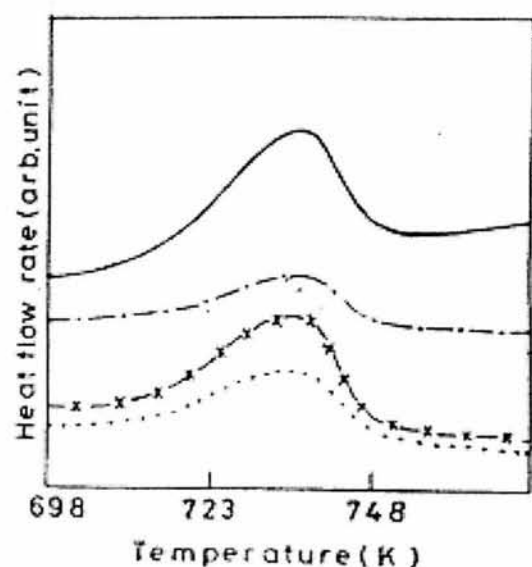


Fig.7 — DSC thermograms of virgin and irradiated  $\text{Ni}_{35}\text{Ti}_{65}$  glass at the heating rate of 20K/min.:— virgin, ..... irradiated at fluence  $1 \times 10^{11}$  ions/cm<sup>2</sup>; -x-x- irradiated at fluence  $1 \times 10^{12}$  ions/cm<sup>2</sup>; -.-.- irradiated at fluence  $1 \times 10^{13}$  ions/cm<sup>2</sup>

system. During thermal treatment, these defects are annealed out well before the temperature necessary for crystallization. Hence, no effect of irradiation is observed.

## 5 Conclusion

We may conclude from the above study that the thermal stability of  $\text{Ni}_{40}\text{Ti}_{60}$  is more than the  $\text{Ni}_{35}\text{Ti}_{65}$ . The high energy heavy ion irradiation does not influence the crystallization kinetics of  $\text{Ni}_x\text{Ti}_{100-x}$  ( $x = 35, 40$ ) glasses.

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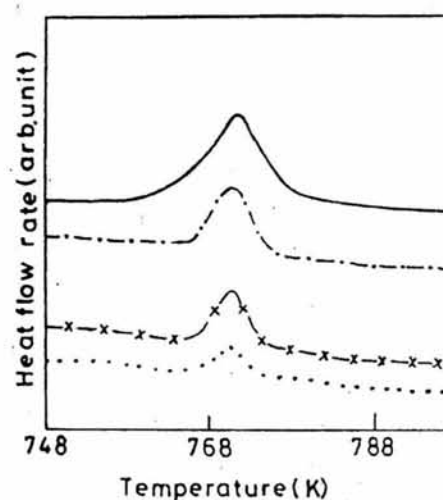


Fig.8 — DSC thermograms of virgin and irradiated  $\text{Ni}_{40}\text{Ti}_{60}$  glass at the heating rate of 20K/min.:— virgin, ..... irradiated at fluence  $1 \times 10^{11}$  ions/cm<sup>2</sup>; -x-x- irradiated at fluence  $1 \times 10^{12}$  ions/cm<sup>2</sup>; -.-.- irradiated at fluence  $1 \times 10^{13}$  ions/cm<sup>2</sup>

permission and providing necessary facilities at the centre.

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