

Crystallization of amorphous $\text{Ni}_{60}\text{Nb}_{40-x}\text{Cr}_x$ alloys

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Crystallization behaviour of amorphous $\text{Ni}_{60}\text{Nb}_{40-x}\text{Cr}_x$ ($x = 0, 5, 10$ and 13 at%) alloys was studied by differential scanning calorimetry and X-ray diffraction measurements. It is shown that the addition of chromium reduces the crystallization temperature, stages of crystallization and activation energies associated with the crystallization stages of the $\text{Ni}_{60}\text{Nb}_{40}$ glass. Crystallization of the $\text{Ni}_{60}\text{Nb}_{40}$ glass occurred in three stages; in the initial stage a metastable M-phase formed in the amorphous matrix as reported earlier [1]. However, contrary to earlier observation [1], M-phase was not very stable and transformed together with some amorphous phase to the equilibrium Ni_3Nb phase in the second stage of crystallization. In the third stage, the remaining amorphous matrix transformed to the equilibrium NiNb phase. On addition of chromium the formation/stability of the M-phase was found to be suppressed and equilibrium NbCr_2 phase precipitated preferentially in the first stage. The second stage, corresponding to the formation of Ni_3Nb phase, remained almost unaltered. The third stage corresponding to the crystallization of NiNb phase disappeared completely at 13 at% Cr. In the fully crystallized samples the proportion of the NiNb phase decreased and that of NbCr_2 phase increased continuously with chromium concentration.

1. Introduction

Metallic glasses are usually in a thermodynamically metastable state and transform into one or more thermodynamically stable crystalline forms on thermal treatment. Many physical and mechanical properties of a metallic glass are altered significantly on crystallization [2, 3]. Knowledge of the crystallization behaviour of metallic glasses is therefore of considerable importance especially when technological applications of glassy alloys are being considered. Few studies have been made on crystallization of metal-metal glasses though considerable work has been done on crystallization behaviour of metal-metalloid glasses [2, 3]. These investigations have revealed that crystallization behaviour is dependent on alloy composition.

The purpose of the present study was to examine the effect of chromium metal addition on the crystallization behaviour of a metal-metal glass, $\text{Ni}_{60}\text{Nb}_{40}$. The crystallization of binary $\text{Ni}_{60}\text{Nb}_{40}$ glassy alloy has recently been investigated in detail [1]. Akhtar and Chandrasekaran [4] have demonstrated that the glassy phase of $\text{Ni}_{60}\text{Nb}_{40}$ alloy can be retained by rapid quenching on addition of chromium up to certain compositions. In this paper we report our investigations on crystallization behaviour and kinetics of crystallization of $\text{Ni}_{60}\text{Nb}_{40-x}\text{Cr}_x$ glasses. The results are compared with the data reported for $\text{Ni}_{60}\text{Nb}_{40}$ glass.

2. Experimental details

Buttons of the $\text{Ni}_{60}\text{Nb}_{40-x}\text{Cr}_x$ alloys were prepared by melting high purity components in a non-consumable vacuum arc furnace under argon atmosphere. The buttons were repeatedly melted to ensure homogeneity. Amorphous ribbons were prepared by the melt

spinning technique [4]. Alloy buttons were cut into small pieces and remelted by induction heating in a quartz nozzle of around 1 mm orifice diameter. The molten metal was ejected on to a rotating polished copper wheel (around 200 mm diameter) using an ejection pressure of pure argon. Ribbons thus obtained were around 20 to 25 μm thick and about 2 to 3 mm wide.

Differential scanning calorimetry (DSC) experiments were carried out on a computerized Du Pont 1090 thermal analysis system. The samples (typically 5 to 10 mg) were placed in copper pans and heated in an argon atmosphere. Heating rates from 5 to 50 K min^{-1} were employed. To ascertain the structural changes associated with the crystallization exotherms observed in the DSC thermograms, glassy samples were sealed in quartz ampoules under a vacuum of around 10^{-4} torr and isothermally annealed for 30 min at various temperatures. X-ray diffraction analyses of the as-quenched and annealed ribbons were made using a Philips diffractometer with $\text{CuK}\alpha$ radiation at a scanning rate of $1^\circ (2\theta) \text{ min}^{-1}$.

3. Results

3.1. As-quenched structure

As reported earlier [4] the as-quenched $\text{Ni}_{60}\text{Nb}_{40-x}\text{Cr}_x$ ($x = 0, 5, 10, 13$ and 15 ; all compositions in at%) alloys are found to be amorphous up to 13 at% Cr. Ribbons of compositions corresponding to $x = 0, 5, 10$ and 13 were therefore selected for crystallization studies.

3.2. Crystallization behaviour

3.2.1. DSC measurements

Typical DSC thermograms of the as-quenched

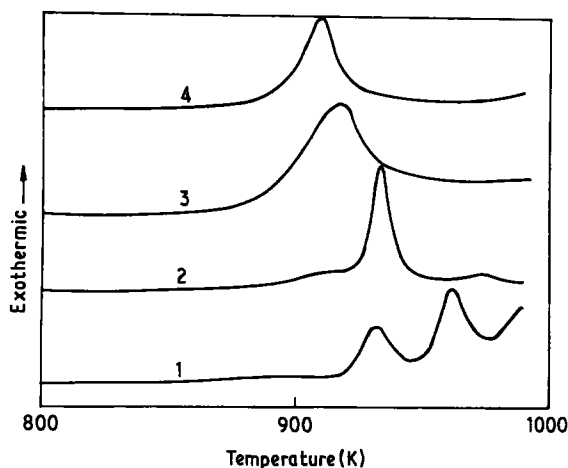


Figure 1 DSC thermograms obtained at a heating rate $\beta = 20 \text{ K min}^{-1}$ for the amorphous $\text{Ni}_{60}\text{Nb}_{40-x}\text{Cr}_x$ alloys: (1) $x = 0$, (2) $x = 5$, (3) $x = 10$ and (4) $x = 13$.

amorphous ribbons are shown in Fig. 1 at a heating rate of 20 K min^{-1} . In $\text{Ni}_{60}\text{Nb}_{40}$ glass crystallization starts at a temperature, T_x , of 921 K leading to three distinct exothermic peaks at 930, 960 and 990 K. The calorimeter was limited to a maximum temperature of 993 K and consequently the third peak is incomplete. A T_x value of 927 K and three exothermic peaks at 940, 980 and 994 K have been reported earlier [1] for the $\text{Ni}_{60}\text{Nb}_{40}$ glass at the same rate of heating. Our observations on $\text{Ni}_{60}\text{Nb}_{40}$ glass are therefore qualitatively in agreement with the reported data though our transformation temperatures are slightly lower.

It is clear from Fig. 1 that the temperature of the start of crystallization, T_x decreases continuously with chromium concentration. For the $\text{Ni}_{60}\text{Nb}_{35}\text{Cr}_5$ glass the first and third exotherms are considerably weaker and the second exotherm is stronger as compared to the $\text{Ni}_{60}\text{Nb}_{40}$ glass. In alloys containing higher concentrations of chromium a single broad exothermic stage is obtained. It should be noted that on addition of 5 at % Cr in $\text{Ni}_{60}\text{Nb}_{40}$ alloy, the gap between the first and second exotherms decreases, whereas the gap between second and third exotherms remains almost unaltered. It therefore appears that in higher chromium concentration alloys the third exothermic event of the $\text{Ni}_{60}\text{Nb}_{40}$ glass has disappeared and the first exotherm has overlapped with the second exotherm leading to a single broad exothermic stage.

3.2.2. X-ray diffraction

In order to ascertain the structural changes associated with the crystallization exotherms observed in the DSC thermograms, glassy ribbons were isothermally annealed for 30 min at various temperatures. Only relevant temperatures depicting different stages of crystallization are described here. Samples of $\text{Ni}_{60}\text{Nb}_{40}$ glass annealed at 873 K revealed sharp diffraction lines superimposed on the broad diffraction maximum of the amorphous material. These lines corresponded to the M-phase observed by Collins *et al.* [1] in the first stage crystallization of $\text{Ni}_{60}\text{Nb}_{40}$. The second crystallization event (annealing at 893 K) was found to be associated with the disappearance of M-phase lines and appearance of equilibrium Ni_3Nb phase lines

superimposed on the broad diffraction maximum of the untransformed amorphous phase. Finally annealing at 923 K yielded a diffraction pattern corresponding to the Ni_3Nb and NiNb phases observed in the equilibrium Ni–Nb phase diagram, and the broad maximum of the amorphous phase disappeared completely. These observations therefore suggest that in the DSC thermogram of $\text{Ni}_{60}\text{Nb}_{40}$ glass the first exotherm corresponds to the crystallization of the amorphous phase into a metastable M-phase, the second exotherm corresponds to the transformation of M-phase and possibly some amorphous phase to the equilibrium Ni_3Nb phase, and the third exotherm corresponds to the crystallization of the remaining amorphous matrix to the equilibrium NiNb phase.

Annealing of $\text{Ni}_{60}\text{Nb}_{35}\text{Cr}_5$ glass samples at 873 K also yielded M-phase together with untransformed amorphous phase in the first stage of crystallization. This behaviour is similar to that observed for $\text{Ni}_{60}\text{Nb}_{40}$. However, the intensity of diffraction lines corresponding to M-phase were weaker in the $\text{Ni}_{60}\text{Nb}_{35}\text{Cr}_5$ samples as compared to the $\text{Ni}_{60}\text{Nb}_{40}$ samples. It implies that addition of chromium suppresses the formation/stability of M-phase. This observation is consistent with the smaller area of the first exotherm and less temperature interval between first and second exotherms of the $\text{Ni}_{60}\text{Nb}_{35}\text{Cr}_5$ glass as compared to the $\text{Ni}_{60}\text{Nb}_{40}$ glass. On annealing at higher temperature (893 K) the M-phase disappeared and diffraction lines corresponding to equilibrium NbCr_2 and Ni_3Nb phases were observed overlapping the broad maximum of the amorphous phase. Finally annealing at 923 K caused complete crystallization of the amorphous phase yielding NbCr_2 , Ni_3Nb and NiNb phases.

In the samples containing higher chromium contents, formation/stability of the M-phase was further suppressed and only the strongest diffraction line of the M-phase could be observed in the first stage of crystallization. Typical X-ray diffractograms depicting crystallization stages in the $\text{Ni}_{60}\text{Nb}_{30}\text{Cr}_{10}$ glass are shown in Fig. 2. Samples annealed at 818 K show only two diffraction lines corresponding to (201) reflection of NbCr_2 phase and (202) reflection of M-phase. Annealing at a lower temperature did not cause any crystallization. This observation suggests that on further addition of chromium, formation/stability of M-phase is further suppressed and NbCr_2 phase precipitates preferentially at the expense of M-phase in the first stage of crystallization (the amount of NbCr_2 phase in the first stage crystallization of $\text{Ni}_{60}\text{Nb}_{35}\text{Cr}_5$ glass was perhaps too small to be detected by X-ray diffraction). On heating at a higher temperature (893 K), the M-phase line disappeared and lines corresponding to Ni_3Nb phase began to appear together with the remaining lines of NbCr_2 phase. Heating at a still higher temperature (923 K) yielded a fully crystalline pattern consisting of equilibrium NbCr_2 and Ni_3Nb phases and the strongest line of the NiNb phase. Thus in the first step M-phase and NbCr_2 phase are formed and in the second step M-phase disappears and Ni_3Nb phase crystallizes. The second step perhaps begins before the first step is completed

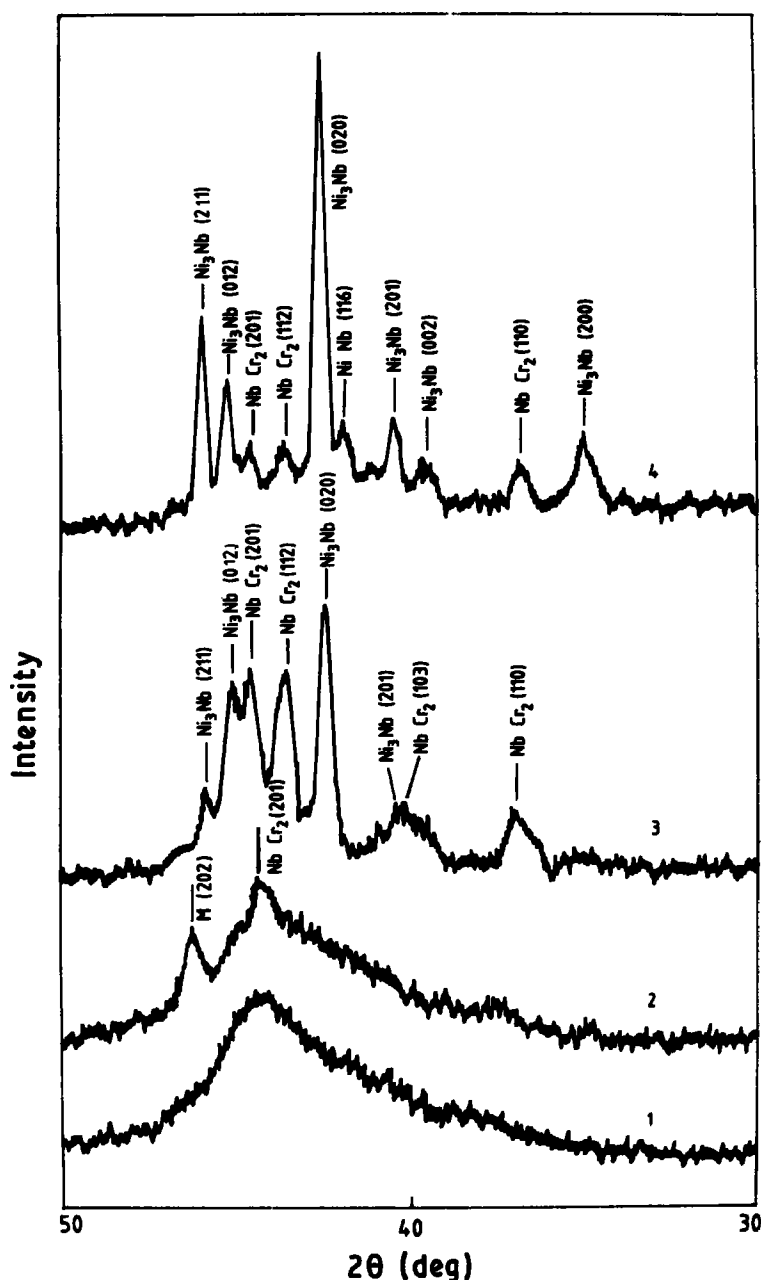


Figure 2 X-ray diffractometer traces depicting crystallization events in the amorphous $\text{Ni}_{60}\text{Nb}_{30}\text{Cr}_{10}$ alloy: (1) as-quenched, (2) annealed 30 min at 818 K, (3) annealed 30 min at 893 K and (4) annealed 30 min at 923 K.

thereby giving rise to a single exotherm in the DSC thermogram. The proportion of NiNb phase in the fully crystallized sample is apparently too small to give rise to a detectable exotherm of the third stage.

On increasing the chromium content progressively the intensity of lines corresponding to the NbCr_2 phase increased and corresponding to NiNb phase decreased in the fully crystallized samples. The crystallization behaviour of $\text{Ni}_{60}\text{Nb}_{27}\text{Cr}_{13}$ alloy was similar to that of $\text{Ni}_{60}\text{Nb}_{30}\text{Cr}_{10}$ alloy. However, no trace of NiNb phase was found in the fully crystallized samples of $\text{Ni}_{60}\text{Nb}_{27}\text{Cr}_{13}$, which contained only NbCr_2 and NiNb phases. In fact, the $\text{Ni}_{60}\text{Nb}_{27}\text{Cr}_{13}$ composition has been found [5] to be eutectic of NiNb and NbCr_2 phases. The decrease in the area of the third exotherm on addition of chromium and its total disappearance in $\text{Ni}_{60}\text{Nb}_{27}\text{Cr}_{13}$ alloy supports our attribution of the third exotherm to the transformation of the remaining amorphous phase to NiNb phase. As chromium is progressively added in $\text{Ni}_{60}\text{Nb}_{40}$ the amount of NiNb phase in the equilibrium alloy decreases and finally diminishes at 13 at % Cr.

3.3. Kinetics of crystallization

DSC thermograms were obtained at different heating rates (β) and the apparent activation energy of crystallization determined using the method of Kissinger [6] from the slope of a plot of $\log(T^2/\beta)$ against $1/T$ where T is the transformation temperature (T_x or peak temperature, T_p). At higher heating rates the third exotherms of $\text{Ni}_{60}\text{Nb}_{40}$ and $\text{Ni}_{60}\text{Nb}_{35}\text{Cr}_5$ glasses (corresponding to the formation of the NiNb phase) were incomplete and variation of the third peak temperature, T_{p3} with heating rate could not be monitored completely. Typical DSC scans for $\text{Ni}_{60}\text{Nb}_{27}\text{Cr}_{13}$ glass at different heating rates are shown in Fig. 3. Figs 4 and 5 show the Kissinger plots of T_x , T_{p1} and T_{p2} for $\text{Ni}_{60}\text{Nb}_{40}$ and $\text{Ni}_{60}\text{Nb}_{35}\text{Cr}_5$ glasses, respectively, and Fig. 6 shows similar plots (T_x and T_p only) for $\text{Ni}_{60}\text{Nb}_{30}\text{Cr}_{10}$ and $\text{Ni}_{60}\text{Nb}_{27}\text{Cr}_{13}$ glasses. Activation energies obtained are also depicted in the figures.

4. Discussion

The T_x and T_p values observed for $\text{Ni}_{60}\text{Nb}_{40}$ glass in the present investigations are slightly smaller than

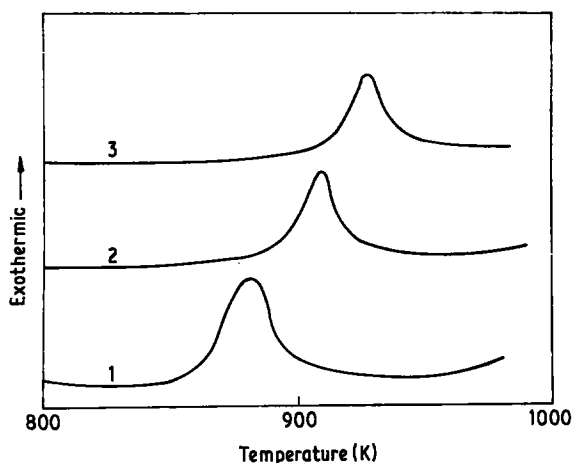


Figure 3 DSC thermograms of the amorphous $\text{Ni}_{60}\text{Nb}_{27}\text{Cr}_{13}$ alloy obtained at heating rates, β , of (1) 5, (2) 20 and (3) 50 K min^{-1} .

those reported earlier [1]. Such small deviations are not unexpected when different calorimeters are used [7] and could also result due to little changes in composition. The decrease in the temperature of start of crystallization, T_x , of the $\text{Ni}_{60}\text{Nb}_{40}$ glass on addition of chromium implies a definite loss in thermal stability. On the other hand, chromium has been found to increase the thermal stability of metal-metalloid glasses [8–12]. The crystallization temperature, T_x , provides only an integrated view of the stability of metallic glasses since crystallization is a complex phenomenon depending on many parameters [13]. Among the variables which influence crystallization behaviour are the mode of crystallization, number of quenched-in nuclei, activation energy for diffusion and the difference in free energy between the amorphous and possible crystalline phases. Many of the above variables may change on chromium addition in the $\text{Ni}_{60}\text{Nb}_{40}$ matrix. As shown in the present investigations, the mode of crystallization has changed on chromium alloying since some crystalline phases resulting on crystallization of chromium-containing

glasses are different from those obtained on crystallization of $\text{Ni}_{60}\text{Nb}_{40}$ glass. A significant decrease in activation energy of crystallization is also established.

In the past there was some question as to the structure of the first phase to appear on crystallization of $\text{Ni}_{60}\text{Nb}_{40}$ glass. Although formation of a tetragonal phase similar to the Ni_2Ta phase found in the equilibrium Ni-Ta system has been reported [14], the present results support the initial findings of Ruhl *et al.* [15] and subsequent observations of Collins *et al.* [1] in which the structure of the metastable phase was identified as being similar to that of the equilibrium M-phase in the Ni-Nb-Al system. In that system the σ -like M is found over a range of low aluminium (≤ 20 at %) composition containing a constant niobium content of approximately 48 at % [16]. Under the nonequilibrium conditions present during the crystallization of the $\text{Ni}_{60}\text{Nb}_{40}$ glass a metastable extension of the ternary M-phase region to the binary Ni-Nb system is observed.

The sequence of crystallization events in $\text{Ni}_{60}\text{Nb}_{40}$ glass observed in the present investigations is not exactly similar to that observed by Collins *et al.* [1]. These authors have reported a four-step crystallization process in which M-phase remains stable up to high temperatures even after the appearance of equilibrium Ni_3Nb and NiNb phases and transforms to these phases in a fourth stage at very high temperatures. However, our investigations indicate that M-phase is not so stable and transforms completely in the second crystallization stage even before diffraction lines of the equilibrium NiNb phase start appearing. Collins *et al.* [1] have suggested that in glassy alloys of higher niobium content (than $\text{Ni}_{60}\text{Nb}_{40}$) a polymorphous transformation of the glass to the metastable M-phase would be expected. In fact it has been observed [17] that amorphous $\text{Ni}_{50}\text{Nb}_{50}$ transforms completely to M-phase prior to transformation to the equilibrium NiNb phase. For alloys of lower niobium content Collins *et al.* suggest that there is no free

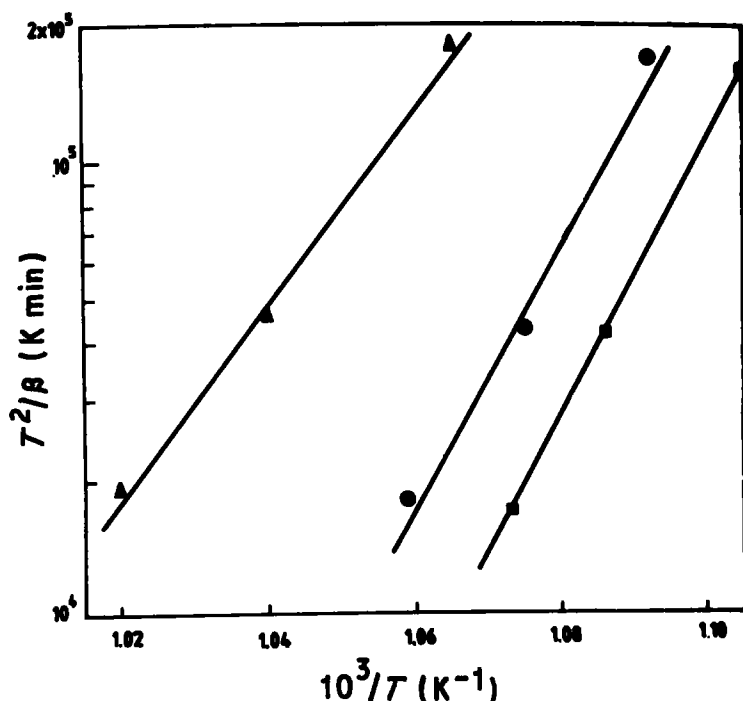


Figure 4 Plots of T^2/β against $1/T$ for crystallization of $\text{Ni}_{60}\text{Nb}_{40}$ glass: T_x (squares) $E \sim 6$ eV, T_{p1} (circles) $E \sim 5.8$ eV and T_{p2} (triangles) $E \sim 4.3$ eV.

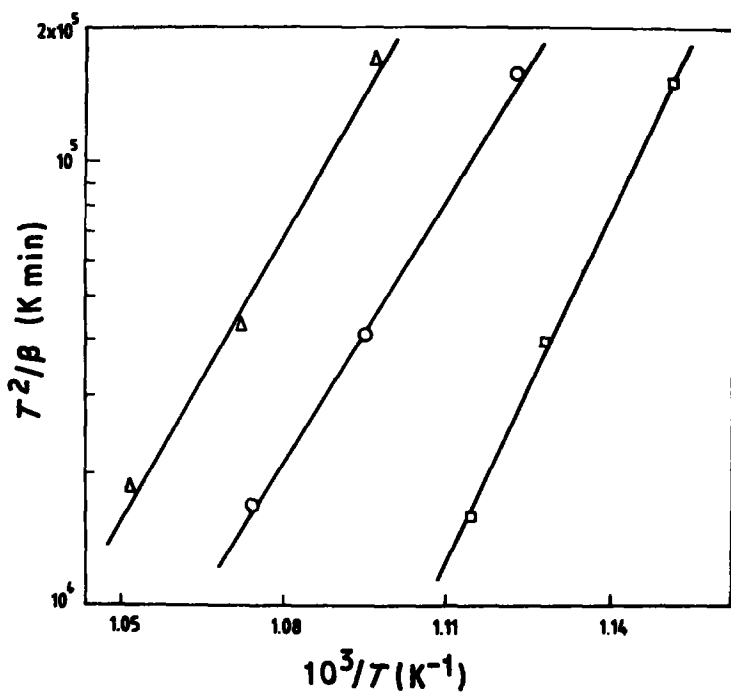


Figure 5 Plots of T^2/β against $1/T$ for crystallization of $\text{Ni}_{60}\text{Nb}_{35}\text{Cr}_5$ glass: T_x (squares) $E \sim 5.1$ eV, T_{p1} (circles) $E \sim 3.9$ eV and T_{p2} (triangles) $E \sim 4$ eV.

energy advantage in the formation of M-phase and alloys should transform to equilibrium phases without initial formation of M-phase. These authors have argued that $\text{Ni}_{65}\text{Nb}_{35}$ glass crystallizes to the equilibrium phases by a two stage process in which a larger fraction of the glass transforms to Ni_3Nb prior to the transformation of the remaining nickel-depleted glass to NiNb phase. In the present case, the $\text{Ni}_{60}\text{Nb}_{40-x}\text{Cr}_x$ alloys become depleted in niobium on addition of chromium, and suppression of the M-phase formation on addition of chromium is in keeping with the above view.

The effective activation energy for the start of crystallization of $\text{Ni}_{60}\text{Nb}_{40}$ glass ($E_x \sim 6$ eV) determined in the present experiments is somewhat lower than the value of ~ 6.3 eV determined by Collins *et al.* [1] and agrees with the value of ~ 6 eV estimated by Pratten

and Scott [18] by constant heating rate DSC experiment. On chromium addition, the value of E_x decreases continuously which is consistent with the decrease in T_x . A significant decrease in the activation energy of the first crystallization step, E_1 , is observed on addition of 5 at % Cr which implies ease of formation of the equilibrium NbCr_2 phase as compared to the metastable M-phase since the first exotherm corresponds to the formation of both phases in $\text{Ni}_{60}\text{Nb}_{35}\text{Cr}_5$ glass. It should be noted that the activation energy of the second crystallization stage, E_2 which corresponds to the formation of equilibrium Ni_3Nb phase changes only marginally on addition of 5 at % Cr. For higher chromium contents, since both the exotherms have overlapped leading to a single broad exotherm, the activation energy change cannot be directly correlated to the formation of different phases. Nevertheless the

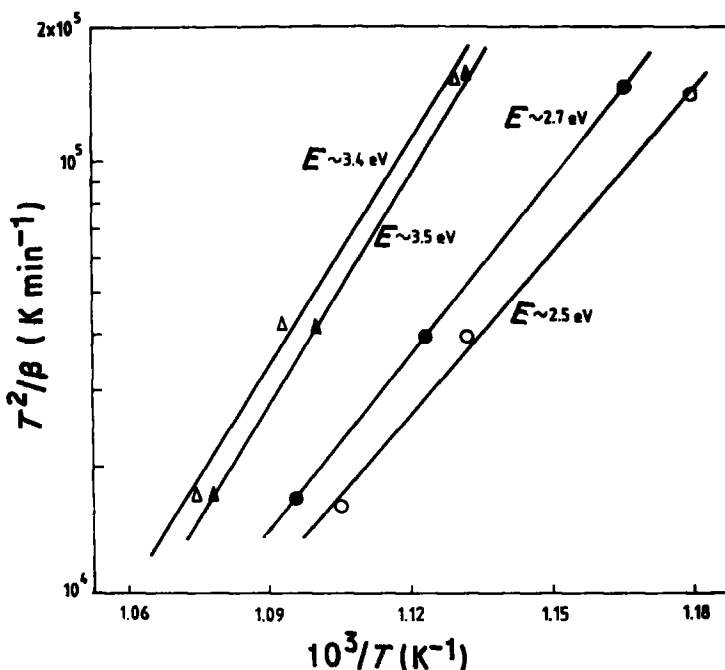


Figure 6 Plots of T^2/β against $1/T$ for crystallization of $\text{Ni}_{60}\text{Nb}_{30}\text{Cr}_{10}$ and $\text{Ni}_{60}\text{Nb}_{27}\text{Cr}_{13}$ glasses: T_x (circles) and T_p (triangles). Open and filled data points correspond to 10 and 13 at % Cr, respectively.

activation energy of crystallization, E , is less in these alloys reflecting further decrease in the stability of M-phase and/or preferential formation of NbCr₂ phase.

5. Conclusions

The Ni₆₀Nb₄₀ glass crystallizes in three stages. In the first stage, the as-quenched glass partially crystallizes into a metastable phase with structure similar to that of the M-phase in the Ni–Nb–Al ternary system. The metastable phase, together with some amorphous phase transforms to the equilibrium Ni₃Nb phase in the second stage. In the third stage the remaining nickel-depleted amorphous matrix transforms to the equilibrium NiNb phase.

Addition of chromium reduces the crystallization temperature, stages of crystallization and activation energies associated with the crystallization stages of the Ni₆₀Nb₄₀ glass. In the first stage, the formation/stability of the M-phase is suppressed and equilibrium NbCr₂ phase precipitates preferentially. The addition of chromium has no significant effect on the formation of equilibrium Ni₃Nb phase in the second stage. The third stage corresponding to the formation of NiNb phase disappears completely at 13 at % Cr. In the fully crystallized samples the proportion of the NiNb phase decreases and that of NbCr₂ phase increases continuously with chromium concentration.

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