

MICROHARDNESS STUDIES OF THE $Te_{50}As_{50-x}S_x$
AMORPHOUS BULK SYSTEM

By

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ABSTRACT

The results of measurements of the microhardness (H_v) on chalcogenide glasses of the $Te_{50}As_{50-x}S_x$ system (where $x=0,11,16,21$ at, wt.%) were reported. The dependence of (H_v) on composition show a drastic decrease in the hardness by the addition of sulphur on the expense of arsenic. It is also found that the microhardness of the ternary system increases with a maximum at the crystallization temperature on isothermal annealing at different temperatures. The glass transition temperature of $Te_{50}As_{50-x}S_x$ glassy composition was identified mechanically.

INTRODUCTION:

The dependence of microhardness on composition of the Sb-Se chalcogenide system⁽¹⁾ shows a monotonic increase with increasing Sb content. The microhardness of the stoichiometric composition of the families of Sb-Se system increases with increasing the annealing temperature.

The microhardness (H_v) of the As-Ge-S chalcogenide system has been determined by studying the microstructure of polished surfaces of samples using a PMT apparatus⁽²⁾. The values of H_v varies from 54.1 to 263. 1 kg/mm² depending on the GE/S ratio. The Vickers hardness

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H_v of the Ti-Nb-Si amorphous alloys was determined by Inoue and Co-workers⁽³⁾. There is a tendency for both H_v and crystallization temperature to increase with increasing Nb content.

Investigations of the microhardness changes during isochronal annealing of amorphous $Fe_{40} Ni_{40} B_{20}$ alloy in the temperature interval 20-1000°C have been performed, showing two maxima in the microhardness⁽⁴⁾.

EXPERIMENTAL

The glass samples in the system $Te_{50} AS_{50-x}S_x$ (where $x = 0, 11, 16$ and 50 at wt.%) were prepared by mixing together the high purity constituents in silica ampoules sealed off at 10^{-5} Torr and heating to 1100°C for 10 hours with continuous shaking to ensure good homogeneity. The melt was then quenched in ice-water. X ray examination of specimens indicated a complete absence of the crystalline state. DTA (Shimadzu DT-30) was used to determine the glass transformation temperature (T_g) and the crystallization temperature (T_{cl}) by using 50 mg of samples in powdered form and heating rate of 20 K/min. A microhardness tester (Shimadzu-Type M) with automatic loading was used. A standard load 50g, with 40 seconds duration and ten impressions for each specimen were selected. The length of the diagonal for each square impression on the surface was measured. The hardness number H_v was calculated using the formula.

$$H_v = 1.854 \times L/d^2 \quad \text{Kg/mm}^2$$

Where L is the applied load, kg and d is the diagonal length, mm

The samples were annealed in a chamber furnace (Heraeus ks 120). The time of annealing was kept constant at 30 minutes. The heat

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treatment was carried out in the temperature range of 50 to 300°C in steps of 50°C.

The thickness of $\text{Te}_{50}\text{AS}_{34}\text{S}_{16}$ sample as a function of the ambient temperature was measured by a dial gauge (type SOMET CSN 251811) connected to the upper point contact electrode. A fine wire chromel-alumel thermocouple in contact with the sample and connected to a digital thermometer (Omega 2168A) was used to monitor the temperature of the sample.

RESULTS

The DTA thermograms of all samples belonging to this system recorded at a heating rate of 20 K/min are shown in Fig. 1. Each curve was characterized by, the glass transition temperature T_g , two exothermic peaks T_{c1} and T_{c2} and only one endothermic peak T_m . The glass transition temperature and the crystallization temperatures are shown in table 1. Fig. 2 shows the change of microhardness associated with the sulphur content. For $\text{Te}_{50}\text{AS}_{50}$ composition, it is noticed that the composition is very hard with $H_V = 178 \text{ kg/mm}^2$. On the addition of sulphur, the hardness decreases drastically to 76 kg/mm^2 for 11% sulphur. On further, the hardness increases very slightly to 88 and 91 kg/mm^2 for 16% and 21% sulphur respectively. As the sulphur content increases to 50% the hardness slightly decreases to 80 kg/mm^2 .

The hardness H_V of the ternary system $\text{Te}_{50}\text{AS}_{50-x}\text{S}_x$ has been determined as a function of the annealing temperature as shown in Fig. 3. It is noticed that the hardness of 11% sulphur increases slightly on annealing at 100°C. An abrupt increase in the hardness occurred at 130°C which is related to the structural changes accompanied with nucleation and crystallization⁽¹⁾. The sudden decrease in H_V above

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130°C may be attributed to the new formed ductile phases⁽⁵⁾ [Fig.3 (a)]

For composition for samples with 16% sulphur, the hardness increases on increasing the annealing temperature up to 150°C [Fig. 3 (b)]. The increase in hardness at a composition of 16% S is greater than that which occurred in the other cases (11% and 21%S). showing that it is the more disordered one^(6,7).

Hardness variation of $\text{Te}_{50}\text{As}_{29}\text{S}_{21}$ showing the behaviour as shown in Fig. 3 (c). The maximum hardness value 189 kg/mm² occurred at 189°C. Above T_{cl} the hardness decreases with increasing the annealing temperature

Dipping of a pin electrode inside a 1mm sample thickness of composition $\text{Te}_{50}\text{As}_{34}\text{S}_{16}$ as ambient temperature increases was used to obtain an idea about the glass transformation temperature T_g . During heating, the depth of the pin electrode was recorded. Firstly, the movement of the pin was very small or negligible, but on reaching a critical temperature 109°C, the displacement becomes very clear with a sudden decrease in the sample thickness (see Fig. 4). This sample temperature is the same magnitude as T_g (108°C) obtained from the DTA thermogram.

DISCUSSION

From the topological properties of the As-Te molecules, the main structure which can be built from two As_2Te_3 pyramids is a chain like structure. In As-rich glasses, the As-As bonds must also be considered. These bonds are responsible for many physical properties. The As-As distance is much smaller than Te-Te one. Therefore, free rotation from the cis position to the trans position cannot take

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place^(8,9) because of the high energy barrier of rotation, these molecules are called locked. Arsenic-pair locks play a crucial role in the melt for two reasons. First, they are able to increase strongly the viscosity of the melt. This is well confirmed in $\text{Te}_{50}\text{As}_{50}$ which has the maximum hardness value at room temperature (178 kg/mm^2). Secondly, As-As bonds are more stable than As-Te and Te-Te bonds⁽¹⁰⁾. This is the reason for the high hardness of $\text{Te}_{50}\text{As}_{50}$.

With the addition of sulphur on the expense of arsenic, As-Te, S-S and Te-Te bonds are developed. The Te-Te bonds become more important leading to the increase of topological disorder in the system and free rotation around the Te-Te axis, accompanied by a decrease in the viscosity. Therefore, the drastic decrease in the hardness of $\text{Te}_{50}\text{As}_{29}\text{S}_{11}$ is related to the presence of Te-Te bonds. The slight increase in the hardness of $\text{Te}_{50}\text{As}_{29}\text{S}_{21}$ could be related to the increase of As-S bonds which are stronger than As-As bonds⁽¹¹⁾. In the binary system $\text{Te}_{50}\text{As}_{50}$ large Te clusters are formed which enhance the ductility and metallic character of such composition accompanied by a decrease in the hardness.

Knowing that the glassy alloys are brittle, on annealing, hardening increases by increasing the ageing temperature up to the glass transition temperature (T_g). This may be attributed to the reduction of the volume-type defects in the host matrix which becomes immobile and increasing the strain energy. The abrupt increase in the hardness by annealing at temperature above T_g could be related to a- The transitions toward more stable forms occur by the minimization of the number of some sort of imperfections. b- The nucleation and growth of new phases (Te and As_2Te_3) with different specific volume. c- Agglomeration of density packing defects which include stress

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centers with high density⁽¹²⁾. The pinning of dislocations or disclinations by defects and precipitates due to the strong interaction of both types induces structural rigidity. The rate of growth of the precipitates increases by increasing the annealing temperature and hence an abrupt increase in the hardness. At the crystallization temperature (T_C), a critical size of the precipitates should exist giving maximum hardness. Also, the structure of the material changes from metastable state into stable crystalline state. On annealing above T_C large precipitates are formed on the expense of the other ones and the material becomes softer (ductile). Also, As_2Te_3 is experimentally not chemically stable at high temperature due to the partially non-covalent nature of the excited As-Te bonds and indeed open air decomposition is observed at temperatures as low as 200°C. Therefore, the amount of crystalline Te phase increases. While the amount of As_2Te_3 decreases. This is well confirmed from the data furnished by x-ray and DTA⁽⁵⁾.

Therefore, the relation between the radius (r_C) of the precipitates and the mean distance (α) between precipitates are used to explain this phenomenon⁽¹³⁾:

- 1- The hardness is proportional to the concentration of dispersed precipitates where $r_C < \alpha$.
- 2- Maximum hardening is obtained when $r_C < \alpha$.
- 3- In overaged alloys $r_C \gg \alpha$.

Finally, we see that the sudden displacement of the upper pin electrode in the sample at the glass transition temperature (T_G) [the glass softening temperature] could be related to the overage character of the chemical bonds in the microscopic structural units such as As-Te covalent chains.

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The thermal treatment results in a tendency to structural equilibrium. We can conclude that annealing at a temperature between T_g and T_c is suitable to improve the mechanical strength of such system.

Table 1:

The glass transformation temperatures and the crystallization temperatures of $Te_{50} AS_{50-x} S_x$ at 20 k/min.

	T_g	T_{cl}
$Te_{50} AS_{50}$	145	224
$Te_{50} AS_{39} S_{11}$	94	126
$Te_{50} AS_{34} S_{16}$	112	151
$Te_{50} AS_{29} S_{21}$	112	180

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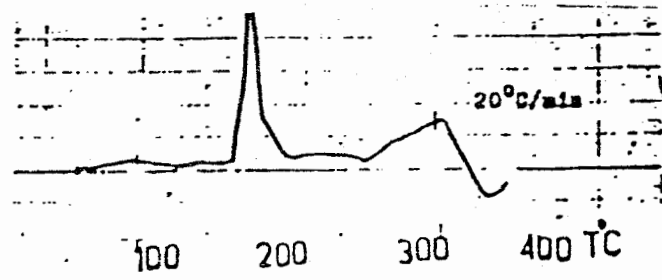
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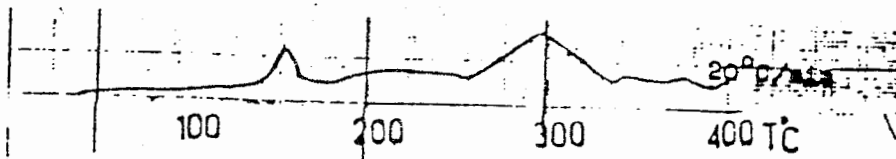
Figure Captions

- 1- The DTA thermograms at a heating rate of 20°C/min. for $Te_{50}AS_{50-x}S_x$ chalcogenide glasses
- 2- Dependence of microhardness on the sulphur content for $Te_{50}AS_{50-x}S_x$ system.
- 3- The hardness of S_{11} , S_{16} , S_{21} as a function of the annealing temperautre
- 4- Sample thickness versus ambient temperature for $Te_{50}AS_{34}S_{16}$ composition

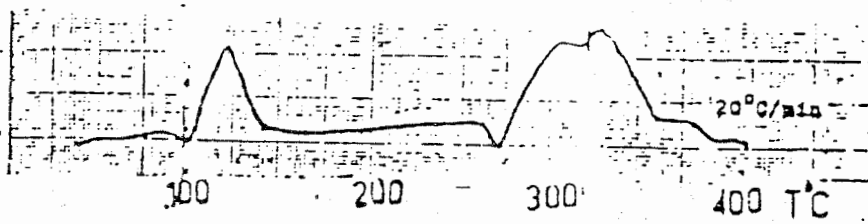
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DTA thermogram of $\text{Te}_{50}\text{As}_{29}\text{S}_{21}$



DTA thermogram of $\text{Te}_{50}\text{As}_{34}\text{S}_{16}$



DTA thermogram of $\text{Te}_{50}\text{As}_{39}\text{S}_{11}$



DTA thermogram of $\text{Te}_{50}\text{Au}_{50}$

Fig. 1

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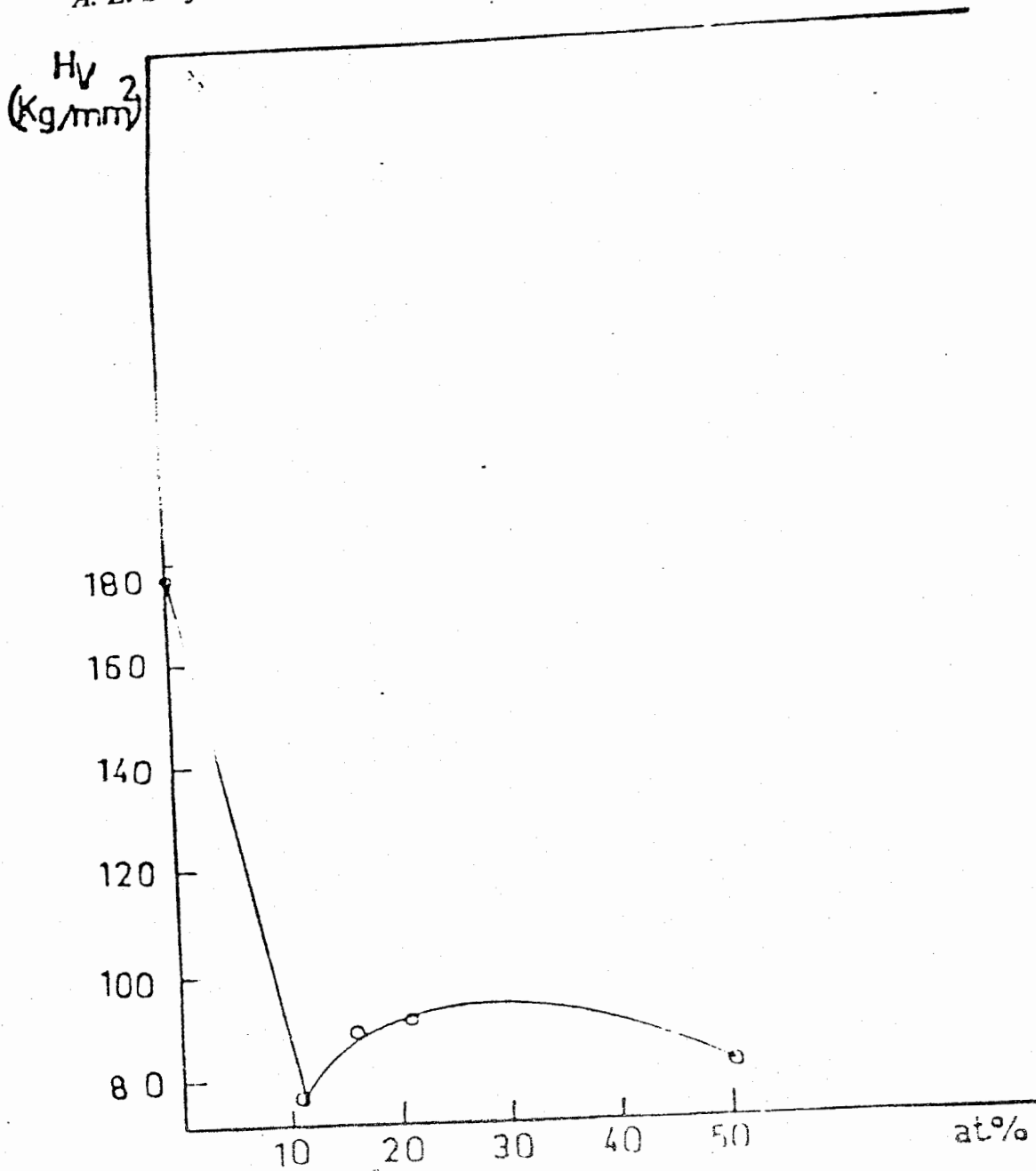


Fig. 2

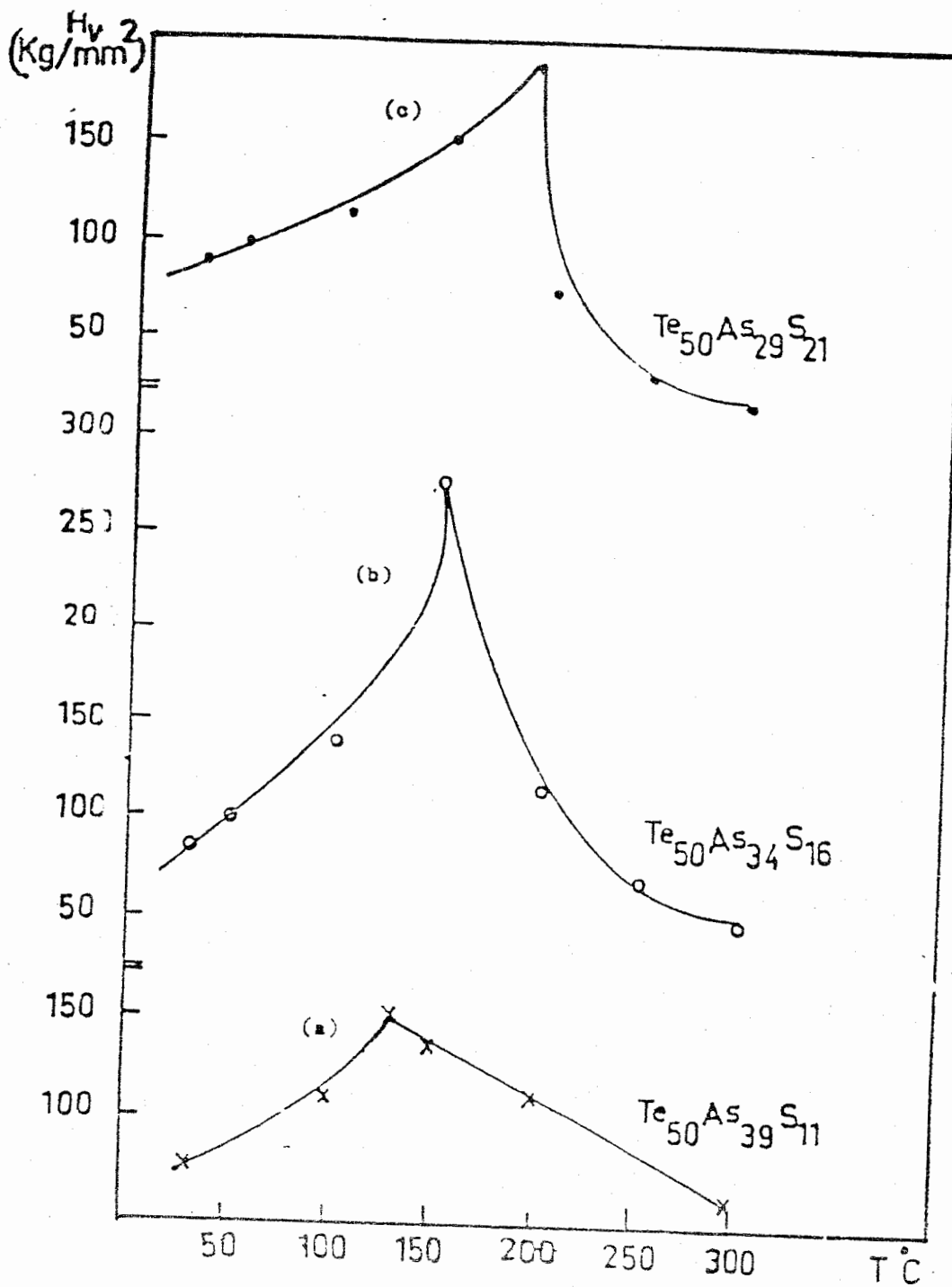


Fig. 3

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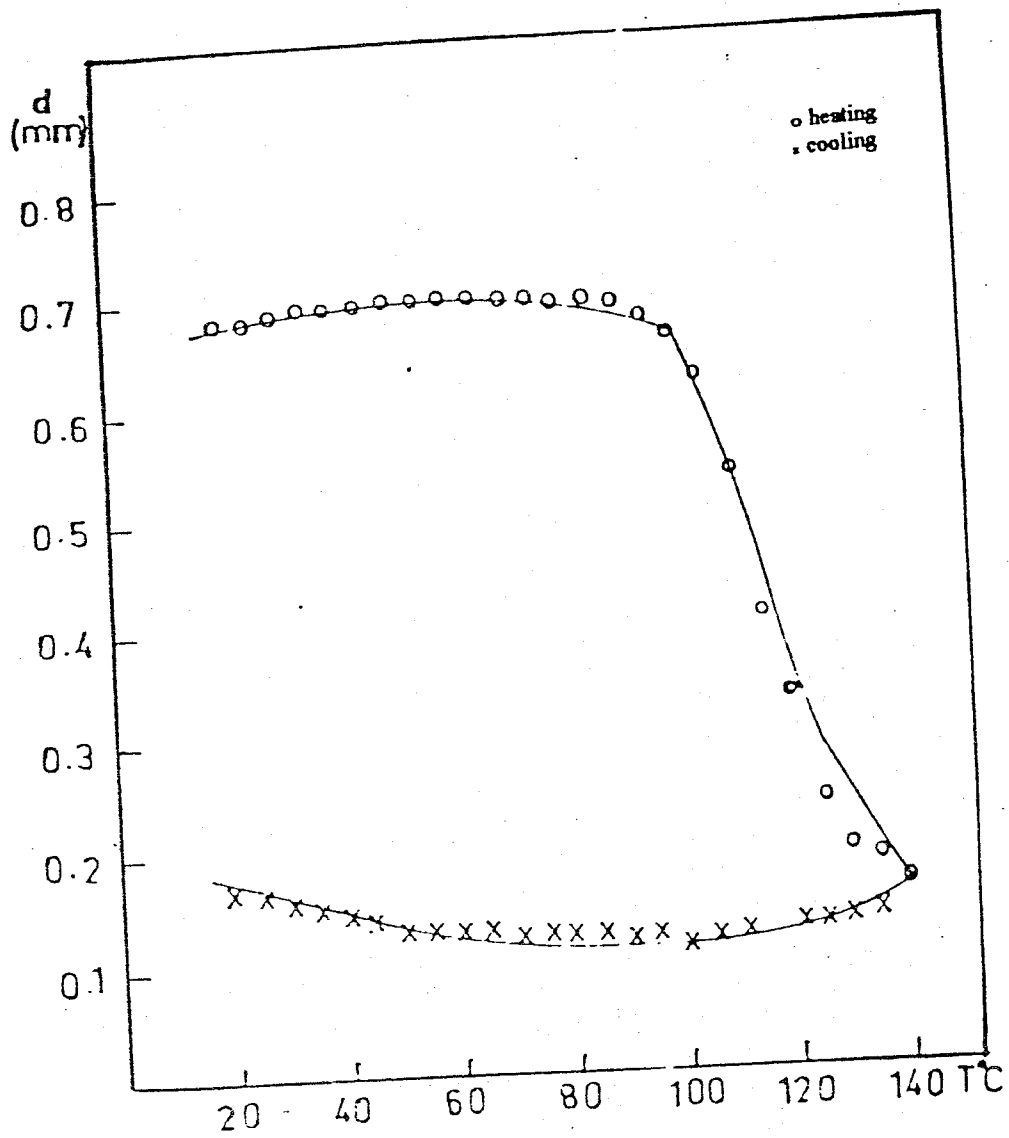


Fig. 4