

Isothermal crystallization on the surface of Te-15at% Ge alloy glass

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Isothermal surface crystallization is investigated for Te-15at% Ge alloy glass. This surface-crystalline pure tellurium nucleates by ageing at low temperature below 451 K. Since germanium-rich phases and GeTe chemical compound prevent this growth, the maximum thickness of the surface layer is below 0.005 mm.

1. Introduction

A metallic glass is transformed into a crystalline one by heating. Two types of crystallization have been found. One of them is observed in bulk [1, 2]. These crystalline particles are sometimes spherical in shape. A second type is that crystals form on the surface [3, 4]. Since various properties are influenced by surface crystallization from the engineering point of view a few works have been carried out [1-5]. However, it is difficult to determine the process of the surface crystal growth. Thus, the purpose of the present work is to investigate the isothermal surface crystallization of Te-15at% Ge alloy glass by the use of thermal analysis.

2. Experimental procedure

Foil samples of Te-15at% Ge alloy glass were prepared by liquid-quenching with a twin-type piston-anvil apparatus under a protective Ar-5% H₂ atmosphere [6, 7]. The purities of constituent materials were 99.99% for germanium and 99.99% for tellurium. Small rectangular pieces (5 mm width × 5 mm length × about 0.06 ± 0.01 mm thickness) of Te-15at% Ge alloy were dipped into an oil bath at a desired temperature controlled within 0.5 K. A rapid cooling and heating apparatus for the ageing was used in this study [1]. The heating and cooling rate of this apparatus are about 10⁴ and 10³ K sec⁻¹, respectively. The

structure of the samples was examined by means of X-ray diffraction and optical observation. The volume fraction of residual glass was measured with differential thermal analysis (DTA) after isothermal ageing.

3. Results

Fig. 1 shows the change in the X-ray diffraction pattern for the specimen with the ageing time at 451 K. Hexagonal peaks of pure crystalline tellurium are found. Considering the X-ray diffraction pattern and optical micrograph, the surface layer is tellurium-rich and crystalline. The lattice constants of these peaks are equal to those of pure crystalline tellurium and are independent of ageing time.

Fig. 2 shows an optical micrograph of a partially crystallized specimen aged for 200 sec at 451 K. A surface crystalline phase is found, together with spherical crystal particles in the bulk. The maximum thickness of the surface layer is measured to be about 0.005 mm in optical observation (Fig. 2), though spherical crystalline particles do not exist near to the growing interface of the surface layer. Since a germanium-rich zone has been reported to exist in front of the tellurium-rich crystal interface [8], the surface crystal growth is deduced to be prevented by the increase in germanium concentration.

The volume fraction of crystalline material is measured by an exothermic peak at T_x (471 K) in the

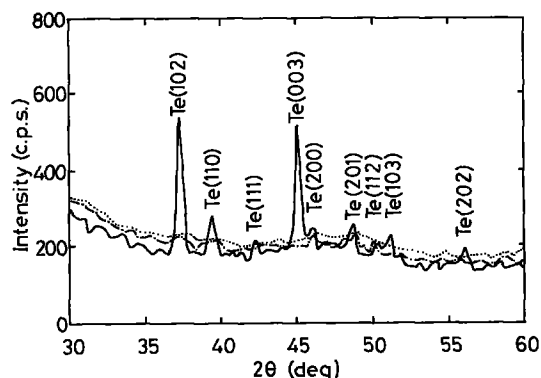


Figure 1 Change in X-ray diffraction pattern with time of Te-15at% Ge alloy glass aged at 451 K: (---) 5 sec, (-·-) 50 sec, (—) 500 sec.

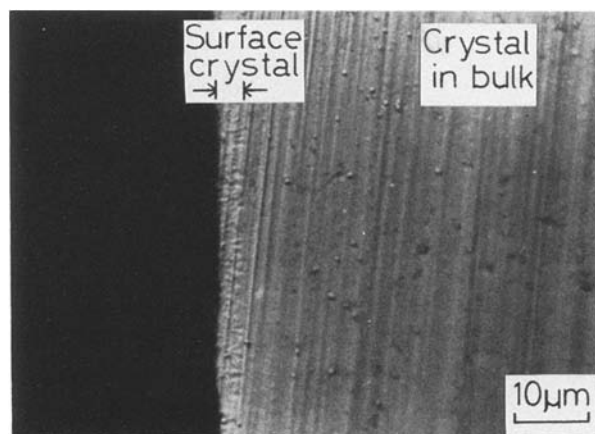


Figure 2 Optical micrograph of partially crystallized Te-15at% Ge specimen aged for 200 sec at 451 K.

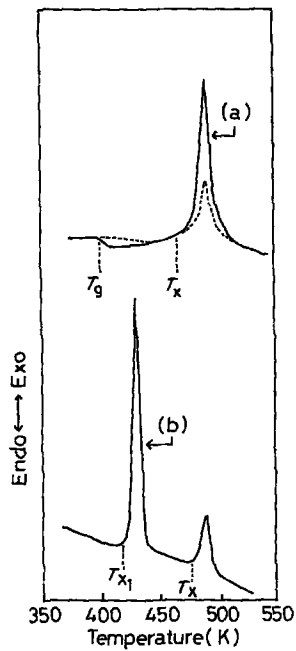


Figure 3 Schematic diagram of DTA analysis of Te-15 at % Ge alloy. (—) (a) as-quenched specimen; (---) partially crystallized specimen aged for 200 sec at 471 K. $T_g = 409$ K, $T_x = 471$ K. (b) Partially crystallized specimens aged for 5 sec at 451 K. $T_{x_1} = 426$ K, $T_x = 487$ K.

DTA. Fig. 3 shows the peaks of an as-quenched glass specimen (solid line) and a partially crystallized specimen aged for 200 sec at 471 K (dotted line). However, another peak is found at a low temperature (426 K) for the partially crystallized specimen aged for 5 sec at 451 K (solid line), as shown in Fig. 3. The sharp exothermic peak at low temperature is supposed to be induced by atom ordering such as crystallization. Since the atom diffusivity is high on the surface, the crystalline material is deduced to form at the surface.

The time-temperature-transformation (TTT) curves of the Te-15 at % Ge crystallization are summarized in Fig. 4. Surface crystallization is found in Region B below 451 K, while the spherical crystalline material is found in Region D (see the spherical crystal particles in bulk in Fig. 2).

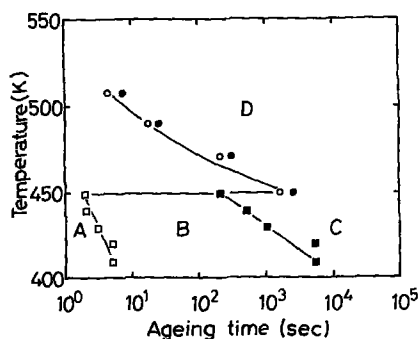


Figure 4 TTT curve of Te-15 at % Ge alloy glass. A: supercooled liquid (no crystal peaks in X-ray pattern, one peak of DTA). B: tellurium surface layer (two peaks of DTA). C: one peak of DTA at T_x . D: spherical eutectic (Te + GeTe) crystal phase in bulk. (○) and (●) are the times at $X = 0.2$ and $X = 0.4$, respectively, where X is the volume fraction of spherical crystals.

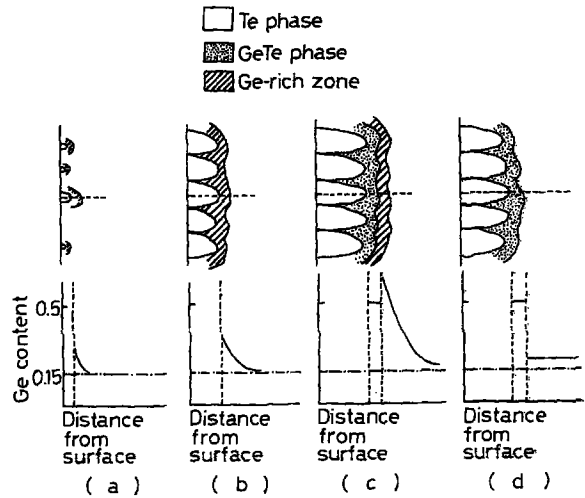


Figure 5 Schematic drawing of crystallization on the surface, together with the change in germanium concentration with distance from the surface of a partially crystallized Te-15 at % Ge specimen. (a) for short-time ageing near the line between A and B in Fig. 4. (b) near the time to maximum heat in Figs 6 and 7. (c) near the line between B and C in Fig. 4. (d) far after the line between B and C in Fig. 4.

4. Discussion

A schematic drawing is suggested for the nucleation and growth of surface crystallization in Fig. 5. The schematic drawing of Fig. 4a is near the line between A and B in Fig. 4. The schematic drawing of Fig. 4c is near the line between B and C in Fig. 4.

The height of the peak at T_{x_1} is large, as shown in Fig. 3 (solid line). The change in heat of the exothermic peak at T_{x_1} with ageing time is shown in Fig. 6. If this nucleation mechanism is dominated by a diffusion-controlled process, the ageing time and temperature enhance the nucleation sites. The obtained heats increase with the ageing time up to the maximum heat of this peak. The maximum heat of this peak at T_{x_1} is 3.5 times larger than that at T_x of the as-quenched specimen. Taking into consideration this result and the volume of the surface layer, the exothermic enthalpy change (about 55 kJ mol^{-1} calibrated by indium, see the maximum values in Fig. 6) at T_{x_1} is larger than that of the pure tellurium (10.7 kJ mol^{-1} [9]) and GeTe chemical compound ($33.47 \pm 10.5 \text{ kJ mol}^{-1}$ [10]).

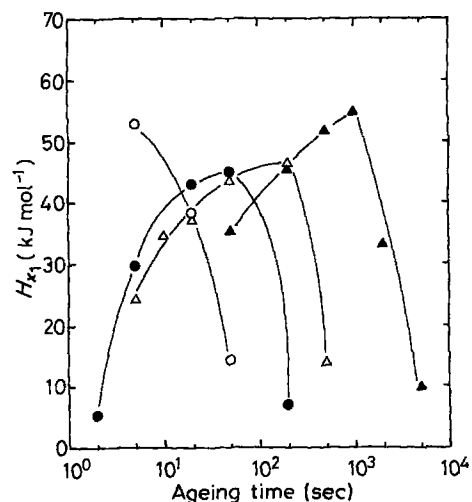


Figure 6 Ageing-time dependence of exothermic heats at ΔH_{x_1} . (▲) 411 K, (△) 431 K, (●) 441 K, (○) 451 K.

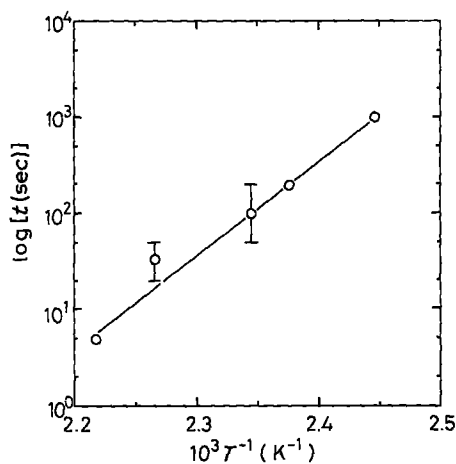


Figure 7 Arrhenius plots of ageing time to maximum heat ΔH_x with the reciprocal of absolute temperature.

The maximum thickness of the surface crystalline layer is about 0.005 mm from the surface (Fig. 2). Since the germanium concentration increases with ageing time in the residual glass near to the growing crystal interface, the growth of the crystalline material is deduced to be prevented by a germanium-rich zone (see Fig. 5a). If the nucleation site is saturated at the maximum values in Fig. 6 (see Fig. 5b), the residual volume of the glass decreases with ageing time after the maximum heat (see Fig. 6). If this assumption is reasonable, the germanium-rich zone and GeTe chemical compound phase exist and prevent the rearrangement of tellurium atoms to tellurium surface crystals, as shown in Fig. 5c.

A straight line is found in the relation between the time to the maximum heats and the reciprocal temperature, as shown in Fig. 7. The apparent activation energy of this process is 193 kJ mol^{-1} . This energy is approximately equal to the activation energy E (196 kJ mol^{-1}) of self-diffusion in tellurium crystals perpendicular to the hexagonal plane [11].

T_x of the aged specimen (see Fig. 3b) is about 16° higher than that of the as-quenched specimen (see Fig. 3a). Since the further addition of germanium atoms enhances the crystallization temperature (T_x) in bulk [13], the increase in germanium concentration with ageing time is indirectly confirmed in the glass, as shown in Fig. 5d. Furthermore, Fig. 8 shows an X-ray diffraction pattern of an aged specimen which is flat-wise polished by the use of a commercially produced water-polishing machine, together with that of the as-aged specimen. Here the depth of the specimen is $0.004 \pm 0.001 \text{ mm}$ and is measured by the use of a roughness meter. The peaks of the GeTe chemical compound are found in the polished specimen. Therefore, tellurium crystal growth on the surface is probably prevented by the increase in germanium concentration at the crystal interface in the glass.

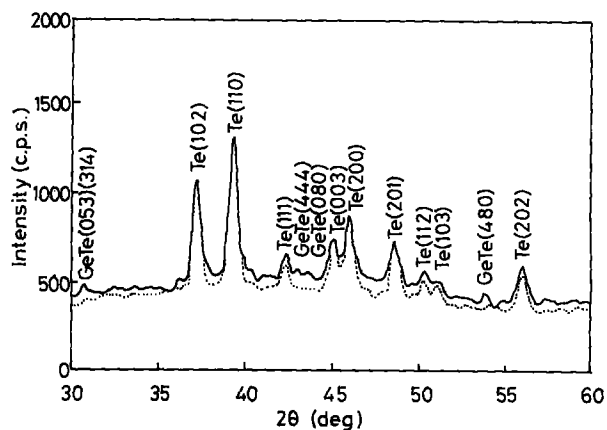


Figure 8 X-ray diffraction pattern of (—) partially crystallized polished specimen ($0.004 \pm 0.001 \text{ mm}$ depth) for Te-15 at % Ge alloy glass; (---) as-aged specimen. 451 K, 200 sec.

5. Conclusion

By the use of thermal analysis, isothermal crystallization on the surface is investigated for Te-15 at % Ge alloy glass. This surface-crystalline pure tellurium, nucleates by ageing at low temperature below 451 K. Since germanium rich phases and GeTe chemical compound prevent this growth, the maximum thickness of the surface crystal layer is about 0.005 mm.

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