Thermal evidence of structural phase transformation in Te–Ge–Sb and Te–Ge–Bi systems

Recently some investigators have taken interest in structural phase transformation observed in chalcogenide crystalline alloys containing Te and Ge, which can easily form a non-crystalline structure after splat-cooling from the liquid state. Most previous investigations have dealt with Te–Ge binary systems. According to the equilibrium diagram, one chemical compound, i.e. GeTe, is present in this system [1]. The structure of crystalline GeTe depends on temperature and on the departure of telluride from stoichiometry. Abrikosov et al. [2] have given the most extensive description of the structure of GeTe; according to these authors, germanium telluride can occur in three polymorphic forms: β, high-temperature cubic structure of NaCl type; α, low-temperature rhombohedral structure and γ, low-temperature rhombic structure.

The kind and sequence of the structural phase transformations as well as their temperatures depend on the composition of alloy. A fragment of the equilibrium diagram of the Te–Ge binary system near the region of germanium telluride homogeneity and the phase transformation regions are shown in Fig. 1. Bierly et al. [3], Chatterjee [4] and Minemura and Morita [5] suggest the reasons underlying the allotropic transformation.

Structural phase transformation has also been observed in Te–Ge–Sn and Te–Ge–Pb systems [6, 7]. These alloys exhibit, above the transformation temperature (T_{tr}), the cubic NaCl-type structure and below this temperature, the rhombohedral structure. The transformation temperature depends on the alloy composition and drops with increase in Sn or Pb content.

Results of investigations of the structural phase transformation in initially amorphous alloys of non-stoichiometric composition Te–Ge–Sn and Te–Ge–Pb (liquid-quenched and then heated), have recently been reported [8]; it was found that the structural phase transformation does not occur in the case of compositions whose glass crystallization temperatures exceed the transformation temperatures, T_{tr}. For example, the values of T_{tr} are: for $Te_{80}Ge_{17.5}Sn_{2.5}$, 563 K; for $Te_{80}Ge_{17.5}Pb_{2.5}$, 550 K. Recently, Parker and Moore [9] have discovered a new compound, $GeTe_4$, in the Te–Ge system; this compound has so far been observed only in alloys crystallized from the glassy state.

Our investigations concerned ternary alloys $Te_{80}Ge_{20-x}Sb_x$ and $Te_{80}Ge_{20-x}Bi_x$ (where $x = 2.5$, 5, 7.5, ..., 20 at.%). These alloys were splat-cooled from the liquid state to a non-crystalline structure. Their calorimetric studies included heating in a Perkin-Elmer DSC-2 microcalorimeter at constant heating rate $\beta = 20$ deg min^{-1}, sensitivity $dH/dt = 5$ mcal sec^{-1} and sample mass $m = 10$ mg. The following thermal effects were revealed by the DSC curves: (i) endothermic glass transition effect (T_g), (ii) exothermic glass crystallization effect $(T_{xo}$ or $T_{xp})$, (iii) endothermic effect which by analogy to alloys Te–Ge–Sn and Te–Ge–Pb can be interpreted as a structural phase transformation [8], and (iv) endothermic melting effect (T_m).

Fragments of the DSC curves which comprise the temperature range of the endothermic effects corresponding to probable structural phase transformations are presented in Figs. 2 and 3. Te–Ge–Bi alloys exhibit two types of endothermic effects. The first type of effect is observed for composition $Te_{80}Ge_{17.5}Bi_{2.5}$; the shape of the curve resembles that found for alloys Te–Ge–Sn and Te–Ge–Pb, and the effect occurs at a similar temperature [8]. This may suggest the transformation of a low-temperature GeTe structure to a high-temperature cubic structure, which occurs during heating of the alloy. The transformation temperature is (as for the Te–Ge–Sn and Te–Ge–Pb systems) lower than the temperature
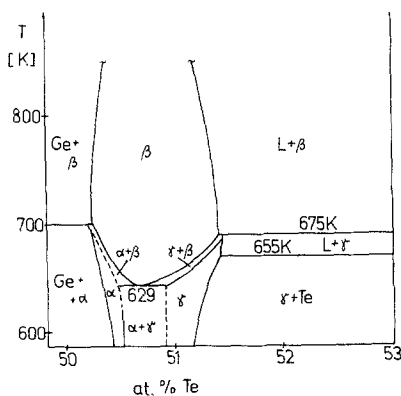

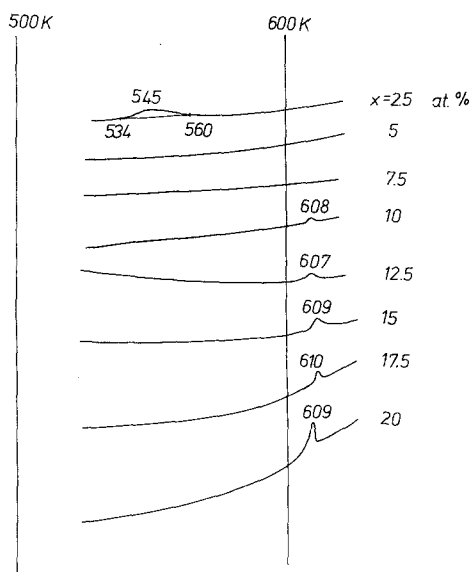*Figure 1* Equilibrium diagram of Te–Ge binary system near the GeTe composition (after [2]).

Figure 2 Fragments of DSC curves illustrating the transformation effects in alloys $Te_{80}Ge_{20-x}Bi_x$.

expected from the equilibrium diagram of Te–Ge binary system (Fig. 1). This points to stabilization of the cubic, high-temperature form of GeTe within a lower temperature range, resulting from the presence of tin, lead or bismuth in the alloy. No effects of the structural phase transformation
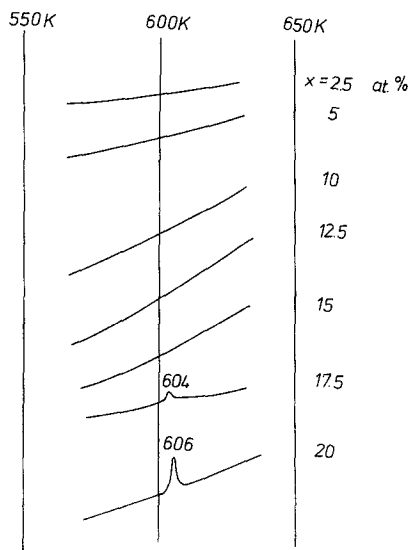

Figure 3 Fragments of DSC curves illustrating the transformation effects in alloys $Te_{80}Ge_{20-x}Sb_x$.

are observed in alloys containing more than 2.5 at % Bi, because in these cases the transformation temperature is lower than the crystallization temperature of the glassy alloys.

The second type of endothermic effect in alloys $Te_{80}Ge_{20-x}Bi_x$ appears at about 609 K, independent of the germanium content. It seems that this effect is related to structural changes of bismuth telluride, Bi_2Te_3, because in alloys containing more GeTe than Bi_2Te_3 no such transformation is observed. With an increase in the content of Bi_2Te_3, the endothermic effect becomes more pronounced; it is most distinct for an alloy containing no germanium, $Te_{80}Bi_{20}$. On the grounds of the similarity between the Bi_2Te_3 and Sb_2Te_3 structures [10–13], we can expect similar changes in the Te–Ge–Sb system. This is confirmed by the endothermic effects appearing for alloys with higher antimony telluride contents ($Te_{80}Ge_{2.5}Sb_{17.5}$ and $Te_{80}Sb_{20}$), also at about 605 K. The fact that the DSC curves exhibit no endothermic effect analogous to that of germanium telluride may suggest that Sb stabilizes the high-temperature cubic structure of GeTe better than Bi. The small content of antimony in the alloy (2.5 at %) shifts the transformation temperature below the crystallization temperature.

Acknowledgement

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Consolidation of diamond powders by thermal decomposition of methane and benzene

Diamond is one of the most difficult materials for sintering, and commercially available sintered diamonds are made under high pressure with addition of foreign metals, e.g. [1, 2]. Vapour infiltration is a well-known method for densification of carbonecious or other materials [3]. It is also reported that diamond can be grown epitaxially on diamond by thermal decomposition of carbon source gases under pressures less than 1 atm [4–7]. The present investigation was undertaken to consolidate diamond powders by vapour infiltration of methane at low pressures. As aromatic hydrocarbons are reported to deposit non-diamond black carbon and to be unsuitable for epitaxial growth of diamond [4], for comparison, benzene was also used instead of methane. The experiments were made primarily for a practical purpose, i.e. to obtain a hard and homogeneous aggregate. As a measure of consolidation, Vickers micro-hardness was measured as a function of a distance from the surface. The hardness of the aggregates obtained was, however, too small to be used practically.

During our investigation, Fedoseev *et al.* [8, 9] applied patents for the same method and used high pressure after carbon deposition to obtain a strong compact which can be used for cutting tools. However, details of the experiments have not been described. The present communication reports the results of our investigation on the vapour consolidation.

A natural diamond powder of 0 to 0.5 μm particle size was prepressed into a disc 5 mm diameter and 3 mm thick at 1000 kg cm^{-2} and then isostati-cally pressed at 2000 kg cm^{-2}. This green compact was infiltrated at 700 to 900° C in three different atmospheres: 1 atm methane, 270 Pa methane, and 1 atm argon saturated with benzene at 15° C. The vapour pressure of benzene at 15° C is 8000 Pa. The weight change during deposition at 1 atm was recorded with a thermobalance. Deposition in 270 Pa methane was made in another furnace equipped with an oil rotary pump. The methane used was of reagent grade (99.95%), and the nominal purity of argon was 99.999%. The rate of flow of the gases was about 20 cm^3 min^{-1}.

The carbon-deposited compacts were cut vertically into two pieces, and the Vickers micro-hardness was measured along the centre axis. The instrument used was a Reihert "MeF 2" universal microscope. The intender load was 100 g, and the load duration was 30 sec.

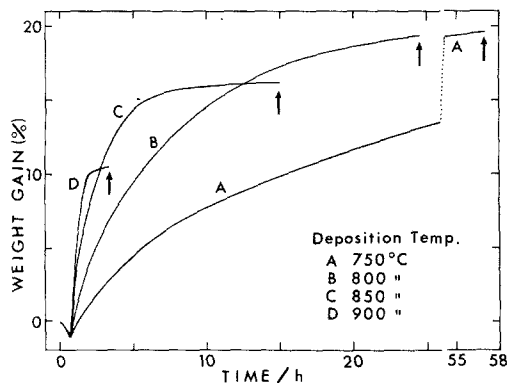Table I summerizes the weights and densities of

Figure 1 Rate of infiltration of diamond compacts with carbon deposited from 1 atm methane. Arrows indicate the times when the compacts were taken out.