Figure 4 TEM micrograph showing a boundary pinned by particles and moving as outlined by the arrow. Note that grain B contains a high density of Al_3Zr particles while grain A is virtually particle free.

reprecipitate in a much coarser distribution has not been established. In both cases the effective Zener drag force will decrease and the effect on the subgrain structure will be an increase in the particle-stabilized subgrain size with increasing strain. This follows from the simple relation above equating the subgrain size to the particle dispersion, r/f. It is emphasized that the dissolution of particles is the primary effect of the imposed hot deformation, and that this reaction stimulates subgrain growth as a secondary process.

This subgrain growth process will be associated with a gradual increase in orientation difference between neighbouring subgrains and there will be no sharp boundary between what can be characterized as a subgrain structure (Fig. 3a) and a distribution of small grains separated by higher

angle boundaries (Fig. 3c). This recrystallization process is analogous to what has been referred to as recrystallization *in situ* or continuous recrystallization [10–12]. Accordingly it is suggested that the present reaction is termed strain-induced continuous recrystallization. It is further suggested that a similar recrystallization reaction accounts for the superplastic behaviour of some of the Zr-bearing aluminium alloys.

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Thermal evidence of overlapping effects of glass transition and crystallization, derived from two different glassy phases in the phase-separated system $Te_{80}Ge_{12.5}Pb_{7.5}$

Interpretation of the calorimetric traces obtained for multicomponent glasses is difficult because of the possibility of a common temperature range for several transformations [1]. In this letter the DSC results obtained for splat-cooled $Te_{80}Ge_{12.5}Pb_{7.5}$

(at.%) glass showing the phase-separation effect are reported. Co-existence of two truly amorphous phases is demonstrated, the glass transition temperature of more stable glass 2 being masked by the crystallization peak of glass 1. Reading of T_{g_2} is possible only after careful pre-heating of the initial sample, which allows crystallization of glassy phase 1.

Fig. 1a shows the DSC-trace for an as-quenched sample. In this case, only one T_g (384.5 K) can be found, and the next two peaks are due to the
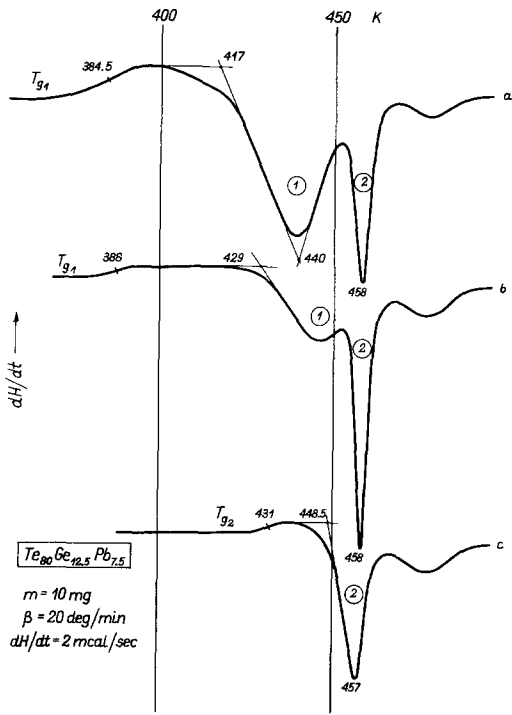
Figure 1 The effect of progress of crystallization of phase 1 on the thermal behaviour of the sample. (a) DSC-trace for as-quenched sample; (b) and (c) DSC-traces for samples pre-heated to 440 K and 450 K, respectively. Desired temperatures 440 K and 450 K correspond to the maximum transformation rate of phase 1 and completion of its crystallization, respectively. Only in trace (c) can T_{g_2} be read.

crystallization effects. After heating the new sample to the maximum temperature of the first peak (440 K), cooling at a rate of $320 \, \text{K} \, \text{min}^{-1}$, and re-heating ($20 \, \text{K} \, \text{min}^{-1}$), there is still a slight T_{g_1} effect (388 K) and a subsequent small crystallization peak 1, the peak 2 location being unchanged (Fig. 1b, Fig. 2 and Table I). After pre-heating the third sample (Fig. 1c) to the temperature near the end of the crystallization range of glass 1 (450 K), cooling ($320 \, \text{K} \, \text{min}^{-1}$) and then re-heating ($20 \, \text{K} \, \text{min}^{-1}$), both T_{g_1} and the crystallization effects attributed to glass 1 completely disappear, i.e. phase 1 becomes crystalline. At the same time (and only in this case) the glass transition temperature of the second glassy phase, T_{g_2} (421 K), can be read. The onset of crystallization peak 2 is then slightly shifted towards lower temperatures.

The manifestation of two glass transition effects indicates the retention in the as-quenched sample of two truly amorphous phases. The question arises as to the nature of these phases. According to the phase diagrams (Fig. 3), the system $\text{Te}_{80}\text{Ge}_{12.5}\text{Pb}_{7.5}$ may be, in fact, considered in the equilibrium as a ternary one composed of species GeTe, PbTe and Te, of average composition $\text{Te}_{60}(\text{GeTe})_{25}(\text{PbTe})_{15}$. Formally, it may also be regarded as a mixture of binaries $\text{Te}_{80}\text{Pb}_{20}$ and $\text{Te}_{80}\text{Ge}_{20}$ at atomic ratio 37.5 : 62.5. Since rapid quenching extends the regions of solid solubility, the initial as-quenched sample could be assumed to
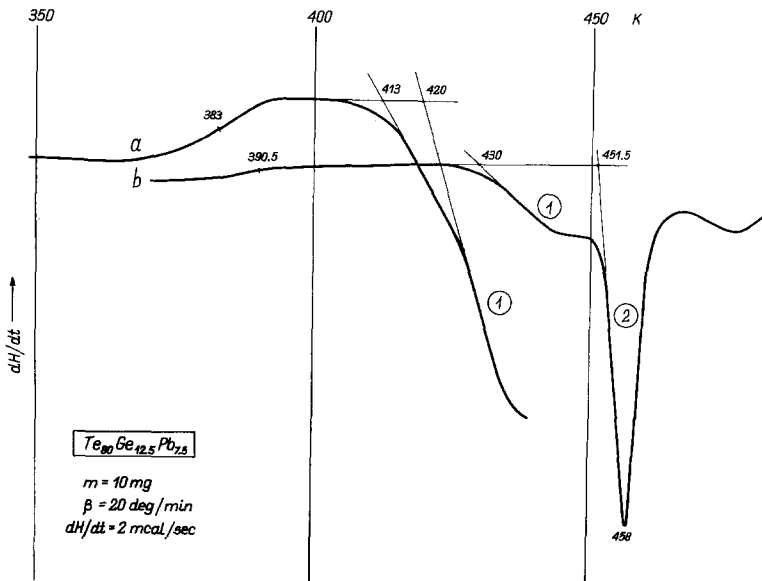

Figure 2 DSC-traces for (a) as-quenched and (b) pre-heated samples used for estimation of the activation energy (chart speed 40 mm min^{-1}).

TABLE I Effect of partial crystallization on the characteristic temperatures of splat-cooled $Te_{80}Ge_{12.5}Pb_{7.5}$ glass. After pre-heating of samples to the desired temperature, they were immediately cooled ($320\,K\,min^{-1}$, to $320\,K$) and then re-heated ($20\,K\,min^{-1}$).

Sample		Glass 1			Glass 2			
		T_{g_1}	T_{x_1}	(K)	T_{g_2}	T_{x_2}	(K)	
		mid-point (K)	Onset	Peak	mid-point (K)	Onset	Peak	
Sample 1	as-quenched	384.5	417	440	b	452	458	Fig. 1a
Sample 2	as-quenched	385	not read	–	–	–	–	–
	pre-heated to 440 K	388	429	a	b	454	458	Fig. 1b
Sample 3	as-quenched	384	413; 420	440	–	–	–	–
	pre-heated to 450 K	no	no	no	431	448.5	457	Fig. 1c
Sample 4	as-quenched	383	413; 420	–	–	–	–	Fig. 2a
	pre-heated to 440 K	390.5	430	a	b	451.5	458	Fig. 2b
Sample 5	as-quenched	386	422	441	–	–	–	–
	pre-heated to 450 K	no	no	no	431	450	456.5	–
Sample 6	as-quenched	382	413; 419	437	–	–	–	–
	pre-heated to 450 K	no	no	no	431	447.5	455.5	–

a: masked by crystallization peak 2,
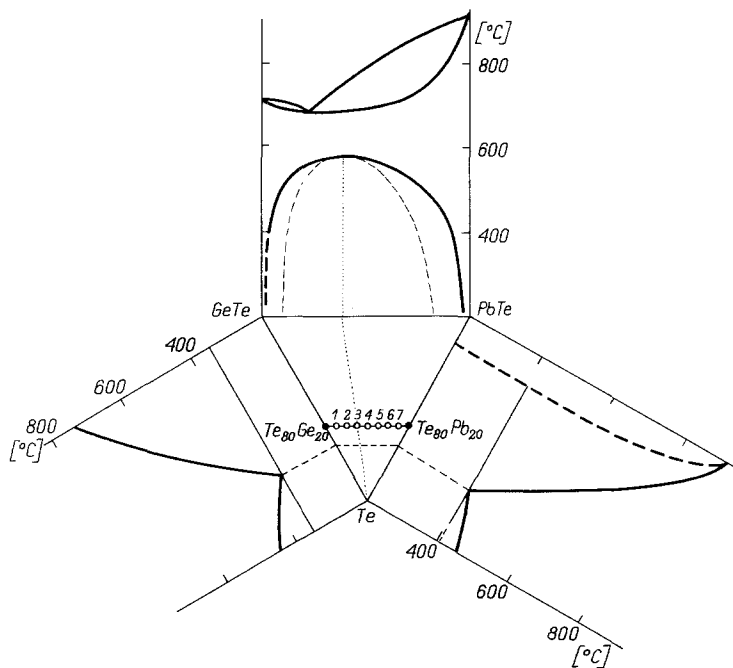b: masked by crystallization peak 1.

Figure 3 Background for discussion of the nature of separated phases in the system studied (denoted as no. 3). Pseudo-binary equilibrium phase diagram GeTe–PbTe is derived from [2]; dashed curve shows the calculated chemical spinodal. Parts of binary Ge–Te and Pb–Te diagrams are taken from [3].

be composed of two super-saturated solid solutions PbTe(Te) and GeTe(Te), or even of PbTe(GeTe, Te) and GeTe(PbTe, Te). Equilibrium solubility of Te in PbTe is much higher than that in GeTe (wide homogeneity range of PbTe compound [3]); therefore, also in the glassy state the excess of Te in solution 1 (PbTe-based) will be greater than in solid solution 2 (GeTe-based). In our previous experiments with Te–A(IV) glasses it has been found that the glass transition temperatures for $Te_{80}Pb_{20}$ and $Te_{80}Ge_{20}$ are 330 K (from extrapolation only) and 435 K, respectively [4]. In the present experiments $T_{g_1} = 384$ K was found for glass 1. This is lower then $T_g = 396$ K estimated by a simple addition rule $(0.375 \times 330 + 0.625 \times 435)$. This indicates that an as-quenched sample cannot be regarded as homogeneous glass of average composition given above. At the same time, the relationship $T_{g_1} > 330$ K may be explained by retention of a certain amount of GeTe in solid solution PbTe(Te). Therefore, glass 1 in fact may be considered to be a solid solution PbTe(GeTe, Te). Since the degree of super-saturation depends on the local cooling rate (and the latter is closely related to the local fluctuations in sample thickness), both T_{g_1} and the shape of peak 1 change slightly from one as-quenched sample to another (Table I). Simultaneously with crystallization of glass 1, precipitation of tellurium may occur, this being manifested by low-temperature branching [5] of crystallization peak 1 (Fig. 2a). On the other hand, the slight shift of T_{g_1} towards higher temperatures is observed for pre-heated samples (runs b in Figs. 1 and 2). This shift known also for glassy polymers is attributed to progressing crystallization [6]. However, an increase in T_g of chalcogenide glasses with pre-heating may also be caused by crystallization of the lower T_g phase of the phase-separated glass [7].

As far as glass 2 is concerned, the very good reproducibility of T_{g_2} (Table I) suggests that glass 2 is not a solid solution, but represents the phase of a strictly defined composition. T_{g_2} (431 K) is very close to the glass transition temperature of $Te_{80}Ge_{20}$ glass (435 K according to [4]). Moreover, glass 2 crystallizes without previous tellurium precipitation. Crystallization peak 2 is narrow and smooth. Therefore, it may be assumed that during the glass-to-crystal transition there is formation –

from glass 2 – of a new metastable crystalline phase, of composition roughly $Te_{80}Ge_{20}$ (i.e. $GeTe_4$). This assumption is also in agreement with the very recently communicated results of X-ray diffraction studies on the crystallization of glassy $Te_{80}Ge_{20}$, which have led to the discovery of compound $GeTe_4$ [8].

Conclusions as to the nature of glasses 1 and 2 were also confirmed by estimation of the activation energies of crystallization, by Piloyan's method [9]. Values of $E_1 = 1.2$ eV and $E_2 = 4$ eV were obtained for glasses 1 and 2, respectively. The high value of E_2 confirms the much more complicated process of new phase formation from glass 2. However, these conclusions ought to be verified by X-ray studies.

Some observations were also made on the influence of crystallinity (or pre-heating) on the crystallization behaviour of glass 2. There appeared the following regularity: the more advanced the crystallization of glass 1, the lower the temperature of the onset of crystallization of glass 2. Therefore, the presence of crystalline phase 1 exerts a de-stabilizing effect on glass 2, as could obviously be expected. This may also be the reason why T_{x_2} (449 K) is lower than the temperature of the onset of crystallization for $Te_{80}Ge_{20}$ glass (466 K according to [4]).

The present results concern only one composition in the ternary system Te–Ge–Pb. However, the nature of the pseudo-binary GeTe–PbTe equilibrium phase diagram (Fig. 3) seems to reflect the tendency to phase-separation in the case of other alloys in this system. Namely, all alloys with the same GeTe:PbTe atomic ratio, and tellurium content $0.5 < x_{Te} < 0.85$ (i.e. compositions along the line connecting the Te-top with the base of the concentration triangle via point No.3), should undergo phase separation, since they exhibit an almost similar spinodal decomposition ability.

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The precipitation behaviour in a thermomechanically treated Al–Zn–Mg alloy

Much work has been done on thermomechanical treatments that involve the combination of plastic deformation and precipitation in aluminium alloys [1–6]. Usually, prior working of the alloy after a solution treatment and quenching operation, was followed by a heat treatment and ageing process. The resultant microstructural changes cannot be considered simply as a dislocation rearrangement plus precipitation. The interaction between lattice defects and the decomposition of the solid solution is characterized by a complex effect. A supersaturated solid solution will, in general, decompose during the ageing process by a multistage reaction path to give a number of intermediate transformation products before the equilibrium phases are established. Vacancies are always an important factor, which together with solute mobility, affect the transformation procedure. In alloys which are plastically deformed, even though new vacancies can be introduced by dislocation interaction, most vacancies can easily migrate to defects such as dislocation cell walls, boundaries and individual dislocations. Thus rapid nucleation and growth of precipitates are always observed on these defects [2, 4]. Holl [1, 2] studied the precipitation phenomenon during the ageing process, in connection with the existence of subgrains in an Al–Zn–Mg alloy. His results indicated that the presence of subgrain structure, produced by 2% tensile strain plus annealing at 450° C for 2 hours, seriously inhibited the hardening at an 165° C ageing temperature. Only coarse, lath-shaped η-phase precipitates were observed at subgrain boundaries and on individual dislocations within subgrains. However, recrystallized specimens which were aged at the same temperature for the same period, produced a dense distribution of fine precipitates within every grain, together with a characteristic precipitate-free zone adjacent to grain boundaries. Holl's work demonstrated the effect of subgrain structure on the precipitation, but further work is necessary to investigate the effects of cold work, annealing temperature and time, since the subgrain formation is directly affected by pre-strain and annealing.

In this letter, an investigation of the precipitation process in an Al–Zn–Mg alloy, for various ageing times at 165° C, is reported. The chemical composition of the Al–Zn–Mg alloy chosen for this experiment is as given in Table I.

Samples in the fully annealed condition were first treated with solution at 465° C followed by water quenching to room temperature and cold rolling to a 50% reduction of area. Subgrains were produced by an annealing process at 400° C for five minutes, and the specimens were aged at 165° C immediately after the annealing treatment. The microstructure of the aged alloy was determined by a TEM thin foil technique, for ageing times up to seven days. Precipitates were found at subgrain boundaries, and on individual dislocation lines inside the subgrains after four hours ageing, as shown in Fig. 1. Most of the precipitates grew to a lath-shaped η-phase ($MgZn_2$). At this stage, no homogeneously distributed small precipitates were

TABLE I

Element	Zn	Mg	Mn	Fe	Si	Cu	Ti	Zr
wt%	4.20	1.55	0.30	0.28	0.14	0.07	0.04	0.13