JOURNAL OF MATERIALS SCIENCE 32 (1997) 1437–1442

Containerless solidification of germanium by electromagnetic levitation and in a drop-tube

D. LI, D. M. HERLACH
Institut für Raumsimulation, Deutsche Forschungsanstalt für Luft- und Raumfahrt, D-51140 Köln, Germany

Containerless solidification of germanium has been realized by electromagnetic levitation and drop-tube processing, respectively. The effect of undercooling in the range of 40–426 K on the as-solidified structures of levitation melted Ge drops (~8.4 mm diameter) was investigated. For undercoolings less than 300 K, the lamellar twins were grown, whereas a microstructural transition to equiaxed grains was observed at undercoolings $\geqslant$ 300 K. Further increasing the undercooling to 400 K, a significant reduction in grain size was achieved. In addition to a similar microstructural development among the particles solidified during free fall in a 8.5 m drop-tube, high-undercooling-induced single crystals were found for some droplets less than 200 μm in diameter. The results on the transition from twins to fine equiaxed grains are accounted for by theories of solidification kinetics and a dendrite break-up model.

1. Introduction

In the theory of crystal growth one distinguishes between two major mechanisms [1]: *lateral growth*, in which the solid–liquid (S/L) interface is atomically smooth except for the presence of ledges or steps, and in which atom transfer from liquid to solid can only occur at a few special sites; and *continuous growth*, in which the S/L interface is assumed to be rough so that atoms can attach themselves uniformly along the interface. It is noted that the smooth versus rough interface classification hinges not only upon the properties of substance in question, such as the entropy of fusion (temperature and composition dependent [2]) and the difference in structure and bonding between the solid and liquid phases, but also upon the driving force for crystallization, namely the undercooling prior to nucleation. This suggests for some materials that solidification proceeds in a lateral mechanism at small undercoolings and undergoes a transition to a continuous growth when a critical undercooling is exceeded. The conceived transition has been directly evidenced by previous experimental work on low melting point materials like phosphorus [3] and gallium [4] of which the critical undercoolings are relatively small and could be readily reached. But as to germanium, a semimetal of a high entropy of fusion, the faceted structure was always grown from the undercooled melt [5], which raises the following questions: does the transition from lateral to continuous growth not exist? or alternatively, is the necessary undercooling for the transition so large that it may be difficult to obtain? Therefore, it is worth making an effort to further undercool elemental Ge through rapid quenching or a proper denucleation technique.

Davies and Hull [6] employed the gun technique of splat-quenching which could bring about a high cooling rate to freeze Ge into a non-crystalline state in very small quantities, but the microstructure of the crystalline phase formed in rapid quenching was not reported. Amorphous Ge was also directly converted from crystalline thin films irradiated by pulsed-laser beam which can give particularly high quench rates [7]. Although the pulsed-laser experiments were facilitated by the distinction of optical and electrical properties between Ge solid and liquid, the dependence of grain structure on the undercooling was not established since the undercooling could not be precisely measured. As is well known, denucleation experiments under slow cooling conditions can offer the benefit of exploring the relationship between the microstructure and the undercooling. Devaud and Turnbull [8] have shown that it is possible to undercool Ge by up to 415 K in droplets of diameter 0.3 to 0.5 mm surrounded by a B_2O_3 flux. $\langle 1\ 0\ 0 \rangle$ twin-free dendrites and grain refinement were discovered at undercoolings $\geqslant$300 K and $\geqslant$ 400 K, respectively. However, with regard to the as-solidified structure they presented, twins were not observed at small undercoolings. Repeatedly, the B_2O_3 flux was utilized to undercool bulk Ge samples in a range of 10 to 342 K [9]. It can be seen that previous studies [8, 9] show some discrepancies in the maximum undercooling attained and in the critical undercooling of the structural transition. Cochrane *et al.* [10] made an attempt to practise

0022–2461

containerless solidification of Ge in a 6.5 m drop-tube. Despite a slight reduction in grain size, there were many straight twin boundaries in a splat sample which they presumed to be of the largest undercooling prior to nucleation. This result seemed to cast doubt on the conversion from twins to refined equiaxed grains for the drop-tube processed Ge. More recently, when high pressure was exerted upon melting–solidification processes of Ge through the pressure–transmitting media B_2O_3, very fine grains of up to $\sim$1.5 μm (but growth morphologies were not shown) and even amorphous phase were reported to be solidified at rather a low undercooling of about 120 K [11]. Obviously, it is not appropriate to simply ascribe the results to undercooling effects, since they should be directly associated with pressure augmenting.

All of the earlier work on undercooling Ge can be summarized briefly as follows: (1) beyond a threshold undercooling, solidified morphology transforms from twins to equiaxed grains; (2) topological metastable phases were possibly induced by extremely high cooling rates or high pressure. With respect to the former, it is desirable to process liquid Ge in a containerless state in order to investigate whether the above-mentioned transition was a general effect of rapid crystal growth, or whether it was particular to the samples as enveloped in flux agents. Another reason for this study was to ascertain whether any metastable phases could be formed in a drop-tube which gives a combination of large undercooling and rapid heat extraction. Therefore, in this paper, the undercooling behaviour and structural evolution have been studied in droplets of Ge using containerless processing, i.e. electromagnetic levitation and a drop-tube.

2. Experimental procedure

The purity of germanium and protective gas used in this work is better than 99.999%. The low electrical conductivity of semiconducting materials at room temperature requires a two-step heating process put forward in reference [12] for electromagnetic levitation melting of germanium. The chamber was evacuated to about 10^{-4} Pa prior to filling with He–20% H_2. An infrared pyrometer recorded the temperature of the sample with an absolute accuracy of ± 5 K through adjusting the emissivity of the pyrometer in order that the displayed melting temperature equalled the actual one, $T_m = 1210$ K. Each levitated sample was subjected to a number of successive heating–cooling cycles before the largest undercooling occurred. More details of the electromagnetic levitation facility are given elsewhere [13].

A recently-built 8.5 m drop-tube was purged to less than 10^{-4} Pa. Under this high vacuum, about 2 g Ge pellets were melted in an alumina-lined graphite crucible placed into an induction coil at the top of the drop-tube, and the successive heating–cooling cycles were repeated three times, in order to evaporate the water vapour and the other surface impurities. During this *in vacuo* treatment, the temperature of the sample can be monitored with an infrared pyrometer. When the vacuum returned to the initial level after the *in vacuo* treatment, the drop-tube was back-filled with helium gas to 70 kPa. The Ge sample was superheated by 300 K for approximately 5 min again, and then dispersed as small droplets in the range of $\sim$20 μm to $\sim$1.5 mm into the drop-tube with argon in a differential pressure of 100 kPa through an orifice about 0.25 mm in diameter in the crucible base. The apparatus was further depicted in reference [14]. There was a definite correlation between the *in vacuo* treatment and the achievement of major undercoolings and the solidified microstructure in the material. Without the *in vacuo* treatment, the undercooling of the melt in the crucible was limited to about 200 K, and the resulting microstructures of particles contained only faceted twins which are thought to be grown at low or moderate undercoolings.

The as-solidified samples were examined with respect to the internal microstructure (etched) and to external surface relief (unetched) by means of optical metallography and a scanning electron microscope (SEM), respectively.

3. Results

3.1. Undercooling behaviour of levitation melted Ge

Measured on levitated bulk droplets of $\sim$8.4 mm in diameter, a typical temperature–time profile, as shown in Fig. 1, consists of four periods: undercooling (un) to a temperature T_n at a cooling rate of $\sim 40\ K\ s^{-1}$ caused by forced convection of He–20% H_2 gas; crystallization leading to a rapid recalescence (nr); a plateau duration, Δt_{p1} during which the remaining melt solidified under quasistationary equilibrium conditions at the S/L interface; and continuous cooling (sf) to ambient temperature. For pure materials undercooled in containerless state, the maximum temperature T_r after recalescence is very close to the melting point T_m, thus assuming $T_r = T_m$ (see Fig. 1). This curve shows an undercooling of $\Delta T = 426$ K which goes beyond the largest one so far reported for small Ge droplets processed in crucibles. In the present work this is because of avoidance of the container-wall induced heterogeneous necleation and establishment of a very clean environment.

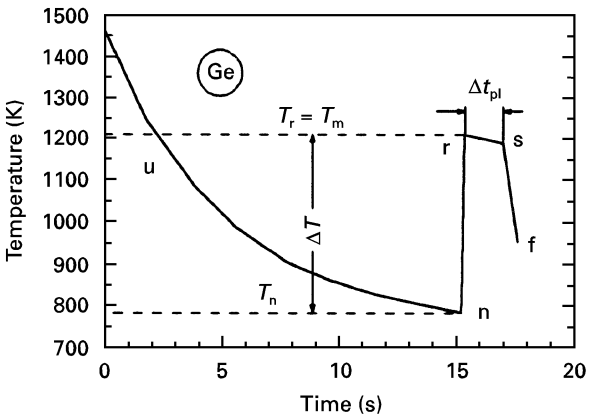


Figure 1 A typical cooling curve of highly undercooled droplets in containerless electromagnetic levitation state. T_n, T_m and T_r represent the nucleation, the melting and the maximum temperature after recalescence, respectively.

3.2 Dependence of microstructures on undercoolings for bulk levitated samples

The microstructure formed at small undercoolings, e.g. $\Delta T = 200$ K, is shown in Fig. 2a. The overwhelming lamellar twins being of faceted features indicate that the lateral solidification mode is dominant. As ΔT was increased to 270 K, the regular lamellar twins were not noticed on the external surface of the sample using SEM. However, the internal structure obviously exhibits twin boundaries; moreover, the equiaxed grains are also seen in the centre of the cross-section (Fig. 2b). When the undercooling exceeds about 400 K, the refined equiaxed grains have a unique growth morphology, just as in some pure metals where twins are absent as a result of continuous growth, as illustrated in Fig. 2c. Throughout a series of samples studied, two critical undercoolings were determined: $\Delta T_{c1} = 300$ K and $\Delta T_{c2} = 400$ K, which divided the solidified microstructure into three regimes: $\Delta T < \Delta T_{c1}$, lamellar twins corresponding to lateral growth; $\Delta T_{c1} \leqslant \Delta T \leqslant \Delta T_{c2}$, coarse grains; $\Delta T \geqslant \Delta T_{c2}$, refined equiaxed microstructure. It follows, based on the above structure examinations, that the solidification mode changes from lateral to continuous at undercoolings larger than 300 K.

3.3. Structural development of drop-tube processed droplets

The structural transformation in Ge particles solidified in the drop-tube is clearly exhibited in Fig. 3. The faceted morphology and twins were grown from a droplet of about 2.5 mm in diameter which was left in the crucible after pressurizing and apparently solidified at a low initial undercooling, as shown in Fig. 3a. The particles (Fig. 3b and c), which had undergone containerless solidification in the drop-tube, remained spheroidal, differing from previous work [10] in which only large droplets more than 1 mm in diameter were yielded. Typically, the microstructure of the drop-tube processed samples is comprised of some equiaxed grains which usually emerged in the centre of the cross-section, and straight twin boundaries of inward radial growth, as shown in Fig. 3b. Furthermore, it appears that nucleation was initiated on the surface, suggesting that the undercoolability was affected by the surface impurities. The droplets are supposed to have undercooled prior to solidification in the vicinity of 300 K, by way of comparison with the structure in Fig. 2b of the samples obtained from electromagnetic levitation process. Not encountered in many droplets, the morphology gave way to completely refined equiaxed grains, as presented in Fig. 3c (the dark line across the section is a crack due to a collision of the particle with the collection pan). It is reasonable to think that the droplet has been undercooled by more than 400 K. The only difference of the microstructure between Figs 2c and 3c lies in grain size; a relatively small grain size appears in Fig. 3c because of a higher cooling rate in the drop-tube. As was expected, the microstructural transformation of drop-tube processed samples is consistent with the results from electromagnetic levitation, and with the observations of Devaud and Turnbull [8] who applied the fluxing method.

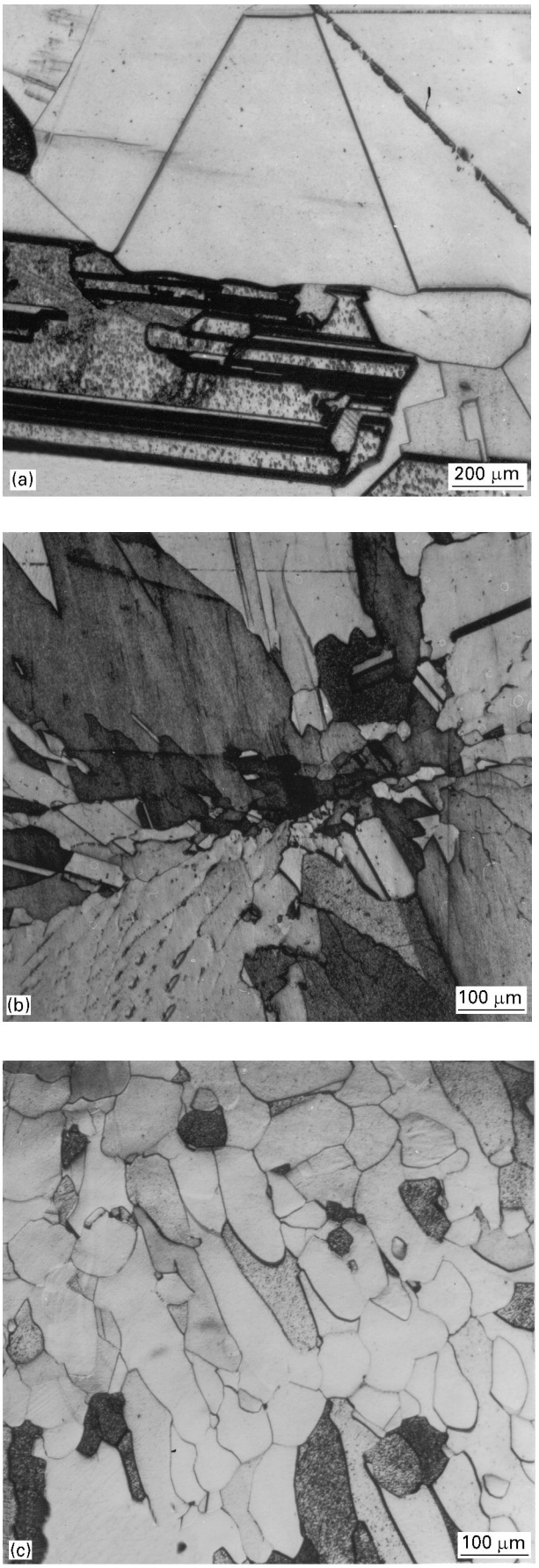
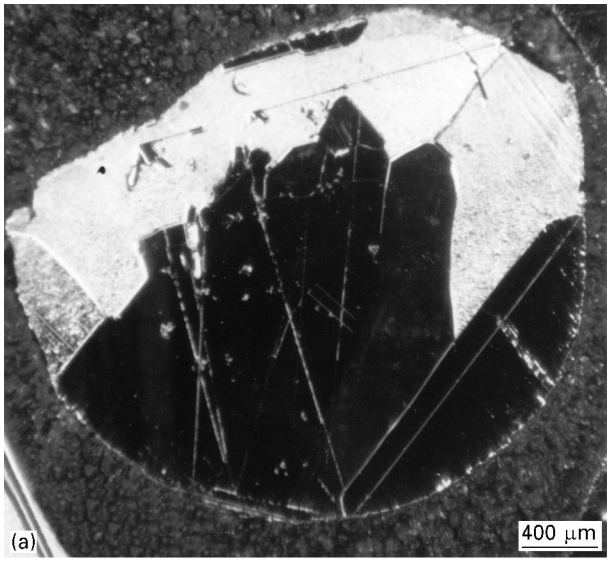
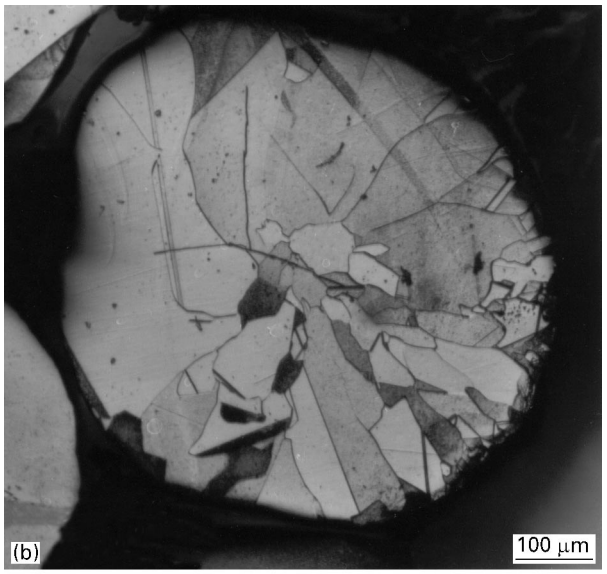


Figure 2 Microstructural morphology transition of levitated samples with the increase of undercoolings: (a) $\Delta T = 200$ K, (b) $\Delta T = 270$ K and (c) $\Delta T = 410$ K.





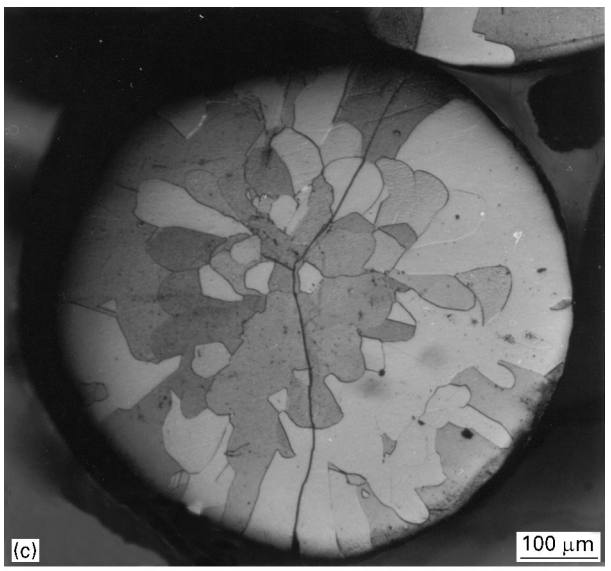


Figure 3 Internal microstructure of (a) a sample which was left in the crucible after pressurizing, and containerlessly solidified particles (b) and (c) in the drop-tube.

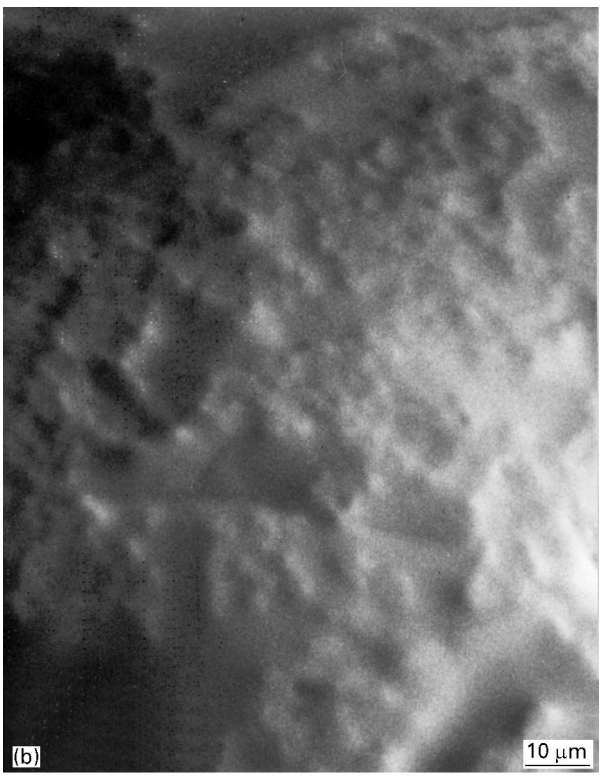


Figure 4 SEM surface relief (unetched) of drop-tube processed particles: (a) an apparent faceted structure, and (b) a rough morphology.

More straightforwardly observing the particle surface relief (unetched) using SEM, we can also acquire useful information about the mechanism of solidification. On the basis of the pronounced edge faces exposed in Fig. 4a, we think that the sample has evidently grown by lateral mechanism at a low undercooling. In a striking contrast, the faceted structure vanished and a rough surface came to light, which

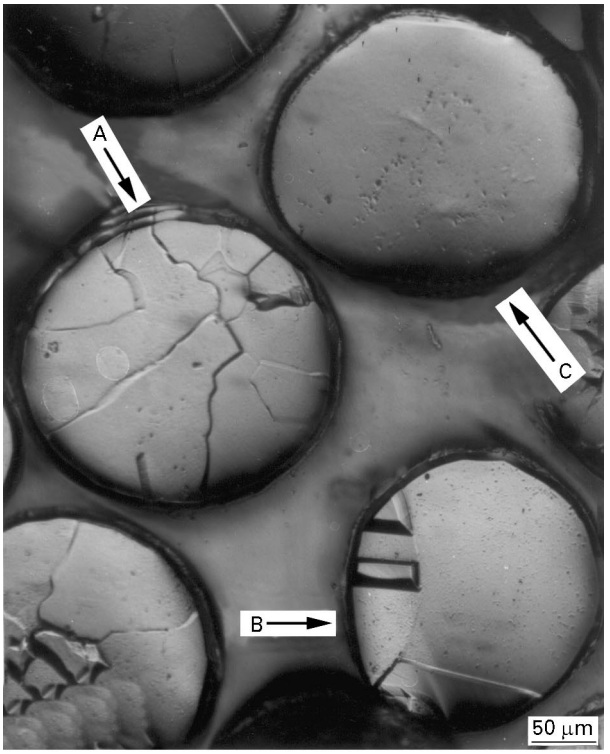


Figure 5 Optical micrographs of the smaller droplets: about ten grains in particle A; only two grains besides a few twin boundaries in B; no grain boundaries observed in particle C, indicating a single crystal.

should be characteristic of continuous growth taking place in highly undercooled Ge droplets, as shown in Fig. 4b.

One of the important observations of the present investigation on the drop-tube processed samples is single crystals formed among the smaller particles. We found that for droplets less than 200 μm in diameter, the number of crystalline grains tends to reduce with decreasing size of particles. In some cases only a few grains together with twin boundaries were discerned (see the particles A and B in Fig. 5). For the other particles, neither grains nor twin boundaries could be observed in the cross-section, indicating formation of a single crystal (droplet C in Fig. 5). It is believed that solidification of the smaller droplets set out at a further larger undercooling than that required for fine-grained polycrystals. Bayuzick *et al.* [15] found that a single crystal was produced in a niobium sample undercooled substantially by 525 K in a 30 m drop-tube. Furthermore, a so-called autonomous directional solidification technique has been recently developed to manufacture a single-crystal turbine blade at high undercoolings [16]. The high-undercooling-induced single crystals resulted obviously from only one nucleation event happening in the melt, and then the dendritic growth front preserved the crystallographic planes with no grain refinement.

In both X-ray diffraction and differential scanning calorimetry analyses on containerlessly solidified samples irrespective of the size or the undercooling, there was no evidence for any crystalline phase other than the diamond cubic structure. For Ge melts of which the temperature was well below the melting point, some metastable phases would be thermodynamically exposed, but they could not be kinetically retained to room temperature owing to a remarkable recalescence.

4. Discussion

4.1. Transition from lateral to continuous solidification

Formation of Ge twins at low undercoolings has been satisfactorily explained by a re-entrant corner model proposed by Wagner [17] and Hamilton *et al.* [18]. The re-entrant corner due to the presence of a twin boundary intersecting the interface will play the most preferable role in atom attachment. However, when the critical nucleation radius is decreased to be comparable to the size of the lateral step, or the fluctuation cluster, as the undercooling rises, any sites will possess similar preference for adsorption of the growth particles. In this case, continuous solidification comes into effect and results ultimately in the dendritic growth morphology and even fine equiaxed structure (see Figs 3c and 4c). A diffuse model [1] regarding the transition of solidification kinetics can also describe the experimental results qualitatively. In accord with the model, the mechanism of the motion of an interface depends on the driving force, i.e. a critical interface undercooling $\Delta T_i^* = \sigma g V_m T_m/(a\Delta H)$, rather than on the nature of the interface, where σ is the interfacial energy, g is the diffuseness parameter, V_m is the molar volume, a is the step height, and ΔH is the latent heat of fusion. The growth modes fall into the lateral growth when the interface undercooling ΔT_i is less than ΔT_i^*, the transitional region ($\Delta T_i^* \leqslant \Delta T_i < \pi\Delta T_i^*$), and the fully continuous growth ($\Delta T_i \geqslant \pi\Delta T_i^*$). Nevertheless, it is difficult to determine ΔT_i^* because of some unknown parameters such as g and a in the formula. Evans *et al.* [19] employed a numerical model for spherical growth to predict ΔT_i^* as 153 K for the transition from lateral to continuous solidification in undercooled Ge. When this value was grafted on to current dendrite growth theories [20], a good agreement between the measured growth velocities as a function of bulk undercooling and the calculated result has been reached [12].

4.2. Application of a dendrite break-up model

At higher undercoolings, two types of Ge droplets processed by electromagnetic levitation or by the drop-tube come about the second microstructural transition to refined equiaxed grains, which proves that grain refinement is a general effect of solidification from largely undercooled melts. Recently, the physical mechanism of this microstructural transformation in undercooled melts has been revealed from experiments and a dendrite break-up model [21]. According to this model, a characteristic time, $\Delta t_{bu} \approx 3R_0^3/(2D_T d_0)$, needed for dendrite break-up of pure materials can be calculated as a function of ΔT, where R_0 denotes the initial trunk radius, D_T the thermal diffusivity and d_0 the capillary length. If Δt_{bu}

is less than the measured isothermal plateau duration Δt_{p1} (see Fig. 1), a grain-refined microstructure should be observed. This implies that the dendrite break-up occurs before the undercooled sample has had time to entirely solidify. A critical undercooling of levitation melted Ge for grain refinement can be estimated as 400 K using the dendrite break-up model, which agrees with the experimental data. However, there is a certain application scope for the dendrite break-up model, like any other theories, namely that this model might not be extended to the following two circumstances. First, it is quite conceivable that the plateau duration Δt_{p1} after recalescence would approach zero at deep undercoolings for very small samples, for instance, for the fine droplets prepared in the drop-tube. In this case, the primary dendrites could be kept without fragmentation, thus leading to the so-called high-undercooling-induced single crystals which have been confirmed by experiments. Second, the recalescence of solidifying melts perhaps does not happen due to fast heat extraction, e.g. in a melt-spinning process. Therefore, there would be kinetic difficulty in the break-up of dendrites formed primarily. However, a fine equiaxed structure in melt-spun Ge ribbons can clearly be observed [22], which is generally attributed to copious heterogeneous nucleation arising from the spinning wheel. It could turn out that the dendrite break-up model is mainly operative for bulk samples under relatively slow cooling environments.

5. Conclusions

We have studied the microstructures solidified from undercooled Ge droplets which were containerlessly processed using electromagnetic levitation and a drop-tube. The maximum undercooling attained in the levitated state was found to be 426 K for bulk droplets. Faceted twins were formed in bulk samples undercooled by less than 300 K. At larger undercooling, i.e. $300 \leqslant \Delta T < 400$ K and $\Delta T \geqslant 400$ K, on the other hand, coarse and refined equiaxed grains were observed, separately. The structural changes reflect a transition from lateral to continuous growth in the highly undercooled liquid. In common with bulk levitated samples, the particles of containerless solidification in the drop-tube have also demonstrated microstructural transformation. Additionally, deeply undercooled melts possibly result in single crystals among the smaller droplets.

Acknowledgements

The authors thank Professor B. Feuerbacher for helpful discussions. One of the authors (D.L., on leave from People's Republic of China) acknowledges financial support from the Alexander von Humboldt-Stiftung, and consistent help from H. Mühlmeyer, K. Eckler, M. Barth, D. Holland-Moritz and J. Alkemper.

References

1. J. W. CAHN, W. B. HILLIG and G. W. SEARS, *Acta Metall.* **12** (1964) 1421.
2. S. N. OJHA and R. K. MANDAL, *J. Mater. Sci. Lett.* **15** (1996) 326.
3. M. E. GLICKSMAN and R. J. SCHAEFFER, *J. Crystal Growth* **67** (1967) 297.
4. S. D. PETEVES and R. ABBASCHIAN, *Met. Trans.* **22A** (1991) 1259.
5. W. A. TILLER, "The science of crystallization: macroscopic phenomena and defect generation" (Cambridge University Press, Cambridge, 1991).
6. H. A. DAVIS and J. B. HULL, *Scripta Metall.* **7** (1973) 637.
7. S. R. STIFFLER, M. O. THOMPSON and P. S. PEERCY, *Appl. Phys. Lett.* **56** (1990) 1025.
8. G. DEVAUD and D. TURNBULL, *Acta Metall.* **35** (1987) 765.
9. C. F. LAU and H. W. KUI, *Acta Metall. Mater.* **42** (1994) 3811.
10. R. F. COCHRANE, P. V. EVANS and A. L. GREER, *Mater. Sci. Engng.* **98** (1988) 99.
11. F. ZHANG and W. WANG, *Appl. Phys. Lett.* **67** (1995) 617.
12. D. LI, T. VOLKMANN, K. ECKLER and D. M. HERLACH, *J. Crystal Growth* **152** (1995) 101.
13. D. M. HERLACH, *Mater. Sci. Engng.* **R12** (1994) 117.
14. W. SOELLNER, "Diplomarbeit in Physik" (Institut für Raumsimulation, DLR, Köln, 1995).
15. R. J. BAYUZICK, W. H. HOFMEISTER and M. B. ROBINSON, in Proceedings of the Hume-Rothery Memorial Symposium: Undercooled Alloy Phases, New Orleans, March 1986, edited by E. W. Collings and C. C. Koch (American Institute of Mining, Metallurgical and Petroleum Engineers, Warrendale, PA, 1987) p. 207.
16. A. LUDWIG, I. WAGNER, J. LAAKMANN and P. R. SAHM, *Mater. Sci. Engng.* **A178** (1994) 299.
17. R. S. WAGNER, *Acta Metall.* **8** (1960) 57.
18. D. R. HAMILTON and R. G. SEIDENSTICKER, *J. Appl. Phys.* **31** (1960) 1165.
19. P. V. EVANS, S. VITTA, R. G. HAMERTON, A. L. GREER and D. TURNBULL, *Acta Metall.* **38** (1990) 233.
20. R. TRIVEDI and W. KURZ, *Int. Mater. Rev.* **39** (1994) 49.
21. M. SCHWARZ, A. KARMA, K. ECKLER and D. M. HERLACH, *Phys. Rev. Lett.* **73** (1994) 1380.
22. D. LI, The Alexander von Humboldt-Stiftung: Report No. 2, 1996 (unpublished).

Received 5 March
and accepted 31 July 1996