JOURNAL OF MATERIALS SCIENCE **34** (1999) 2049–2056

Growth velocity-undercooling relationships and microstructural evolution in undercooled Ge and dilute Ge-Fe alloys

S. E. BATTERSBY*, R. F. COCHRANE, A.M. MULLIS†
Department of Materials, University of Leeds, Leeds LS2 9JT, UK
E-mail: met6am@sun.leeds.ac.uk

A melt encasement (fluxing) technique has been used to systematically study the velocity-undercooling relationship in samples of pure Ge and Ge doped with 0.01 at % Fe at undercoolings up to 300 K. The apparatus was designed such that it was possible to view the sample throughout the experiment, allowing solidification velocity measurements to be made. These velocity measurements were subsequently correlated with the as-solidified microstructure. From a combination of growth velocity measurements and microstructural characterisation it was possible to identify a change in growth morphology from faceted to non-faceted growth in both the pure metal and the dilute alloy. This transition occurred at a lower undercooling in the dilute alloy ($\Delta T > 150$ K) than in the pure metal ($\Delta T > 170$ K). Spontaneous grain refinement was also observed at $\Delta T > 210$ K in Ge-Fe and at $\Delta T > 270$ K in pure Ge. These transitions are discussed and a mechanisms for the change in growth morphology with small amounts of impurity is suggested. © *1999 Kluwer Academic Publishers*

1. Introduction

Rapid solidification has long been known to result in the formation of non-equilibrium structures. Such metastability may take the form of structural refinement, the production of novel crystalline or amorphous phases and extended solid solubility. Rapid solidification has traditionally been achieved by employing rapid quenching techniques. However, the requirement that one dimension of the specimen be small in order to achieve rapid removal of the enthalpy of crystallisation from the solid-liquid interface makes direct observations of nucleation and growth phenomena difficult in these methods. Rapid solidification can also be produced by inhibiting heterogeneous nucleation, allowing a bulk sample to be cooled, in the liquid state, below its equilibrium melting point (undercooling). In this case, the undercooled melt acts as a heat sink, with the result that solidification occurs adiabatically. Consequently, much larger samples may be employed and, provided heterogeneous nucleation can be inhibited effectively, large undercoolings may be achieved and maintained in the melt, without the need for rapid quenching. These large, stationary samples lend themselves to quantitative measurements of growth velocities and the elucidation of the mechanisms of microstructural evolution during rapid solidification. Heterogeneous nucleation may be inhibited by applying containerless processing techniques such as electromagnetic levitation and melt fluxing.

The covalently-bonded structure of germanium restricts the amount of grain growth that will occur during cooling in the solid state subsequent to solidification. Thus, in examining microstructural effects due to non-equilibrium solidification, germanium is a good material to study. Billig [1] described how, at low undercoolings (~10 K), growth in germanium proceeded by the propagation of ledges, that is, it exhibits a faceted growth morphology, where the re-entrant corners of twin planes provide favourable sites for atomic attachment at the otherwise atomically flat interface.

Devaud and Turnbull [2] studied small samples, 0.3–0.6 mm in diameter, covered with a thin layer of flux, heated and cooled in a silica hemisphere, obtaining maximum undercoolings of 415 K. Lau and Kui [3] undercooled samples, 7–11 mm in diameter, to a maximum undercooling of 342 K employing a B_2O_3 flux. In this case the sample and flux were melted and solidified whilst contained within an evacuated glass tube. On the basis of microstructural evidence, both of these authors conclude that a transition from stepwise growth at a faceted interface to continuous growth at a non-faceted interface occurs at a value of ΔT below the critical undercooling, ΔT^*, at which a general grain refinement is observed. Changes in preferred

* Now at British Aerospace plc., Sowerby Research Centre, PO Box 5, Filton, Bristol BS12 7QW.
† Author to whom all correspondence should be addressed.

dendrite growth direction are also well documented [4–6] and are found to be a function of undercooling. For $\Delta T < 60$ K, dendrites grow in the {110} direction changing to the {211} direction as the undercooling is increased, until twin-free {100} dendrites are found once the change in growth morphology from faceted to non-faceted has occurred. Of further interest is the effect of a small amount of solute upon growth morphology and the critical undercooling required for grain refinement to occur. It was found that the addition of 0.39 at % Sn to Ge allowed equiaxed microstructures to be observed at $\Delta T > 250$ K compared to $\Delta T > 300$ K in pure germanium [2].

Growth velocity measurements have been made in levitated Ge and Ge-Sn samples, by Li *et al.* [7], using the increase in output from two silicon photdiodes to measure recalescence times. At a maximum undercooling of 426 K they recorded growth velocities of ≈ 1 m s^{-1}, although the growth velocity was found to be a sensitive function of alloy concentration, with the addition of 0.39 at % Sn increasing the maximum velocity fivefold.

2. Experimental

Undercooling experiments were performed within a stainless steel vacuum chamber evacuated to a pressure of 5×10^{-5} mbar and backfilled to 500 mbar with N_2 gas. Samples were heated, in fused quartz crucibles, by induction heating of a graphite susceptor contained within an alumina shell. Viewing slots were cut in the susceptor and alumina to allow the sample to be viewed through a window in the chamber. Melt encasement, within a high purity glass flux, was employed to reduce the number of potential heterogeneous nucleation sites allowing the attainment of high undercoolings. Temperature determination was by means of a *k*-type thermocouple positioned beneath the crucible, which had been thinned at the base so reducing the thermal lag between the sample and thermocouple. Cooling curves were obtained with the aid of a chart recorder. A schematic diagram of the experimental apparatus is shown in Fig. 1. By heating the sample to its melting temperature, cooling and repeating this procedure, it was found that melting temperatures were reproducible to within ± 5 K. On heating, the sample and flux were taken to 250 K above the melting temperature and held for two hours to ensure complete melting of the glass, encasement of the sample and the removal of gas bubbles from the flux. The samples were subsequently cooled to a predetermined temperature before nucleation was triggered by touching the sample surface with a thin alumina needle.

The measurement of growth velocities was performed using a 16 element linear photodiode array, allowing the time taken for the bright recalescence front to move across the relatively dark sample to be measured. Light from the sample was passed through a beam splitter which distributed the light between a CCD camera and the photo-diode array. The CCD camera allows accurate sample positioning and focusing. It was also possible via this arrangement to measure directly the dimension of the sample along the photo-diode axis. A current proportional to the light intensity falling on each photo-diode is produced which was then amplified and recorded. Each of the 16 photo-diodes has an independent fast settling, low noise, DIFET amplifier with a current to voltage gain of 10^6 VA^{-1}. The signals are then passed, via switching circuitry, to a pair of voltage adders for output. The output signal is displayed as light intensity vs. time trace on a digital storage oscilloscope from which the time taken for the solidification front to move through the sample could be measured.

Samples of Ge were obtained from ALFA (Johnson Matthey) in the size range 3–5 mm and were of 99.9999% purity. Three different fluxes were used: a basic soda-lime glass and two custom fluxes (G1 & G2), which contained 10% and 20% B_2O_3 respectively to lower their softening temperatures. The custom fluxes were made using high purity raw materials, again supplied by ALFA (Johnson Matthey). Compositions for all three fluxes are shown in Table I, together with their

TABLE I

Flux	SiO_2	CaO	Na_2O_3	B_2O_3	Al_2O_3	MgO	T_{sf}/K
Soda-Lime	0.726	0.046	0.152	0.008	0.017	0.036	968
G1	0.6	0.1	0.2	0.1	N/A	N/A	946
G2	0.5	0.1	0.2	0.2	N/A	N/A	917

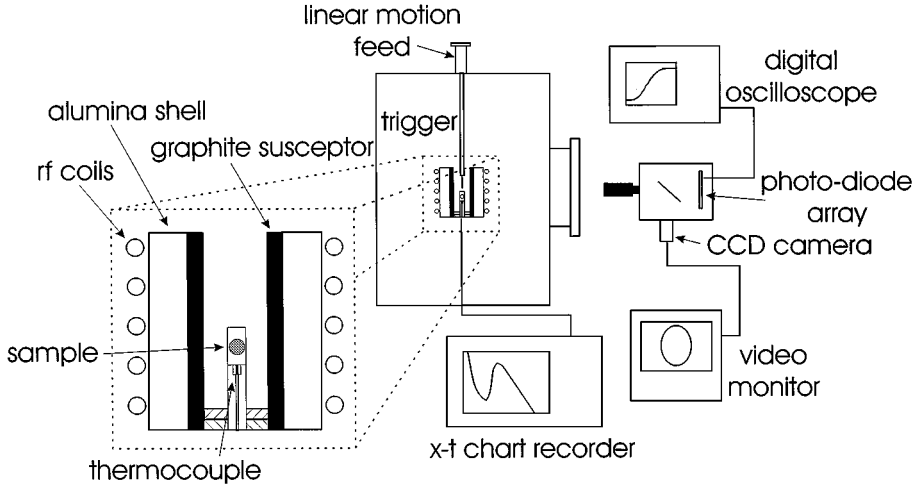


Figure 1 Schematic diagram of the apparatus used to perform undercooling experiments described in this work.

softening temperature (viscosity $= 10^{6.8}$ Pa · s), measured using a standard fibre extension technique.

Dilute Ge-Fe alloys were made in situ in the fluxing apparatus by doping the glass flux with Fe. During the holding period at which the sample and the encasing flux were at elevated temperature the Fe diffuses into the liquid Ge. All Ge-Fe alloys were doped using the same batch of Fe rich flux resulting in a reproducible Fe concentration in the as-solidified alloy of 100 ppm.

Microstructural analysis of the as-solidified samples was performed by optical and electron microscopy. Samples were cold mounted in an epoxy resin, polished and etched in Mukramis reagent. These were then examined using a Nikon optical microscope in differential interference contrast (D. I. C.) mode. Microstructural examination was also carried out using a Philips CM20 transmission electron microscope operating at 200 kV fitted with LINK EDAX analysis facility. To examine crystallite orientation within samples, pole figure plots were generated using a Phillips APD 1700 system 2 automated texture diffractometer using CuK_α radiation. The angle of reflection chosen was for the {111} planes. Samples were sliced equatorially through the nucleation point so that it would lie on the circumference of the pole figure plot.

3. Results

Recalescence velocity measurements as a function of undercooling for both pure Ge and Ge-Fe are shown in Fig. 2. Two main observations can be made about these data sets. Firstly, despite the very low levels of Fe present, recalescence velocities for Ge-Fe are significantly and consistently faster than those for pure Ge for undercoolings less than 250 K. Above 250 K it appears that the two curves may approach one another or even cross, but in the absence of data for the Ge-Fe system above this undercooling no definite conclusions can be drawn. Secondly, for each data set the velocity undercooling curve can be divided into three regimes each of which, as we shall discuss, corresponds to a distinct microstructural morphology. At low undercoolings ($\Delta T < 170$ K in Ge, $\Delta T < 150$ K in Ge-Fe) growth velocities are sluggish and appear to increase approximately linearly with increasing ΔT. As the undercooling is increased further ($170 < \Delta T < 270$ K in Ge, $150 < \Delta T < 210$ K in Ge-Fe) growth velocity begins to increase rapidly. Within this region, the relationship between growth velocity and undercooling can be approximated by a power law. Finally at the highest undercoolings ($\Delta T > 270$ K in Ge, $\Delta T > 210$ K in Ge-Fe) there is a distinct break in the power law relationship.

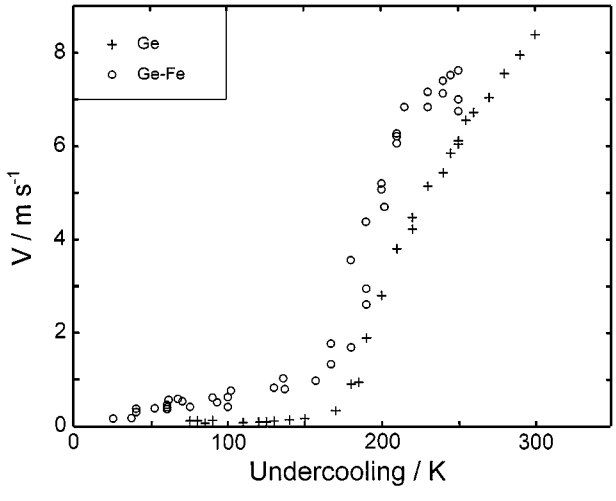
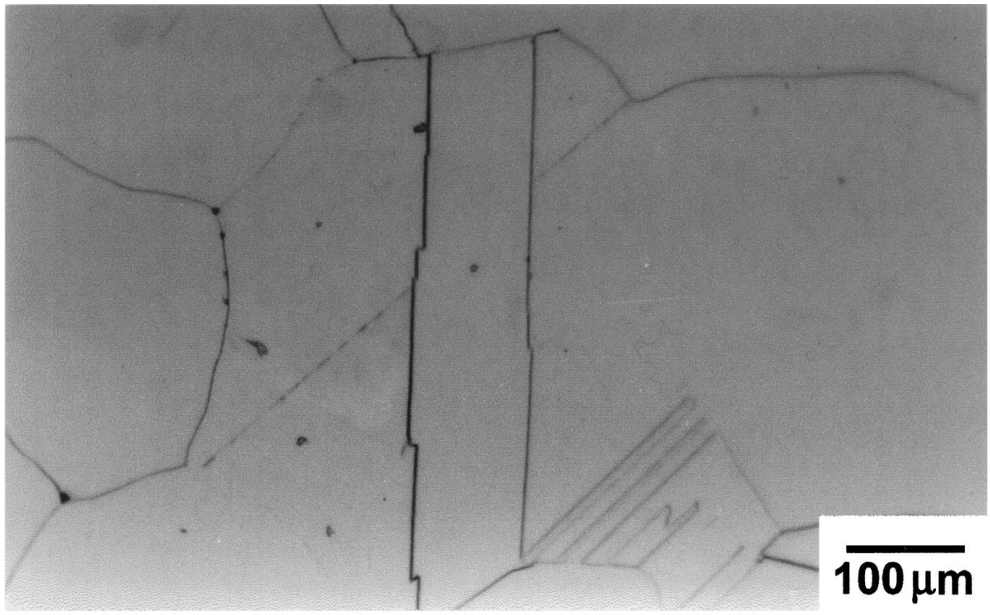


Figure 2 Measured recalescence velocities in pure Ge and Ge doped with 0.01 at % Fe.

As described above, for both pure Ge and Ge-Fe three distinct regimes of microstructural development were identified, which may broadly described as being faceted dendritic, continuous dendritic and grain refined. Faceted dendritic growth occurred in the undercooling range $\Delta T < 170$ K in Ge and $\Delta T < 150$ K in Ge-Fe. Typical microstructures for Ge and Ge-Fe are shown in Figs 3a and b. In both cases the grain structure is very coarse and there is a large density of growth twins apparent throughout the microstructure. However, in Ge-Fe, due to the presence of the solute, it was also possible to see the dendritic substructure (Fig. 3b). The substructure is a well connected dendritic network and is observed to extend throughout the grains. Twinned growth was confirmed by TEM analysis (Fig. 4) and by generating pole figure plots along the {111} direction, as illustrated in Fig. 5 for Ge-Fe. This plot contains reflections from one complete twin grain. The set of poles belonging to the crystal, twinned in a {111} orientation, are numbered 1 to 7 on the plot, where pole 1 is the common pole between the two sets {1, 2, 3, 4} and {1, 5, 6, 7}. Each of the poles 1–6 has a common angle of either 72°53′ or 109°47′ with pole 7.

At higher undercoolings ($170 < \Delta T < 270$ K in Ge, $150 < \Delta T < 210$ K in Ge-Fe) the microstructure still consists of a network of coarse grains, but growth now appears to proceed without twinning. Fig. 6 shows an optical micrograph of the microstructure of a Ge-Fe sample of undercooled by 170 K prior to nucleation. The grain size is quite coarse but the large density of twins previously seen is no longer evident. Furthermore, the connected dendritic substructure observed in Fig. 4 has started to break up in some regions. Fig. 7 shows the pole figure for this sample, the four {111} poles are identified by measuring angles between poles, confirming that this is an untwinned structure.

At the highest undercoolings, another change in microstructure was observed. Samples nucleated at temperatures within this region consisted of fine, equiaxed grains (Fig. 8). The dendritic substructure has broken down completely such that in the centre of the grains, a small, cross-shaped dendritic fragment can be seen (Fig. 9). Pole figure plots generated for a sample undercooled by 250 K confirm that the strong texture previously observed is no longer evident (Fig. 10). These grains are randomly oriented as their distribution throughout the pole figure plot is quite even, there is no clustering around certain areas of the plot as would be expected for oriented grains. This would indicate one of two possibilities—that a large number of dendrites has grown from the melt or that the existing dendrites, as seen in the pole figure plot in Fig. 7, have broken



(a)

(b)

Figure 3 (a) Coarse grained, twinned microstructure observed in Ge-Fe at low undercoolings ($\Delta T = 100$ K). (b) The presence of 100 ppm of Fe delineating the well connected dendritic substructure.

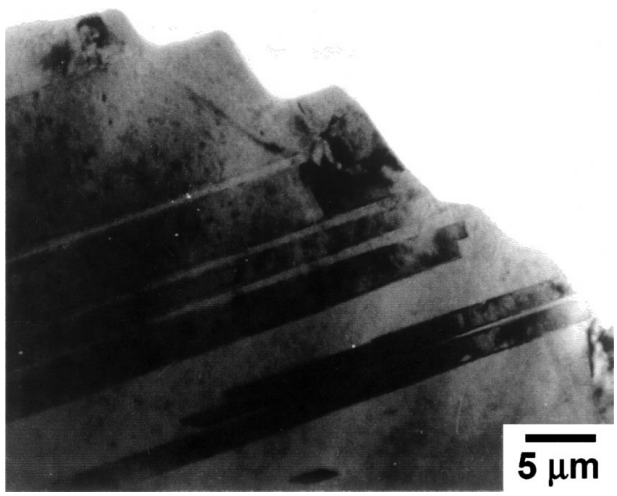


Figure 4 TEM micrograph of Ge-Fe ($\Delta T = 100$ K). A high density of growth twins are present in the sample.

up to form randomly—oriented fragments which act as the nuclei for these grains.

4. Discussion

It is generally believed that in metals the interface between the liquid and crystal is diffuse, providing many sites for atomic addition. Consequently, growth only requires small kinetic undercoolings. Stepwise growth from a faceted interface requires much higher kinetic undercoolings. At low undercoolings, germanium has a faceted interface, the attachment of atoms being aided by growth twins whose presence is required to provide re-entrant corners for atomic attachment. It is suggested that at high undercooling, the interface becomes kinetically roughened, such that a change in growth mode could be observed. Cahn [8] proposed a diffuse interface model where the transition from lateral

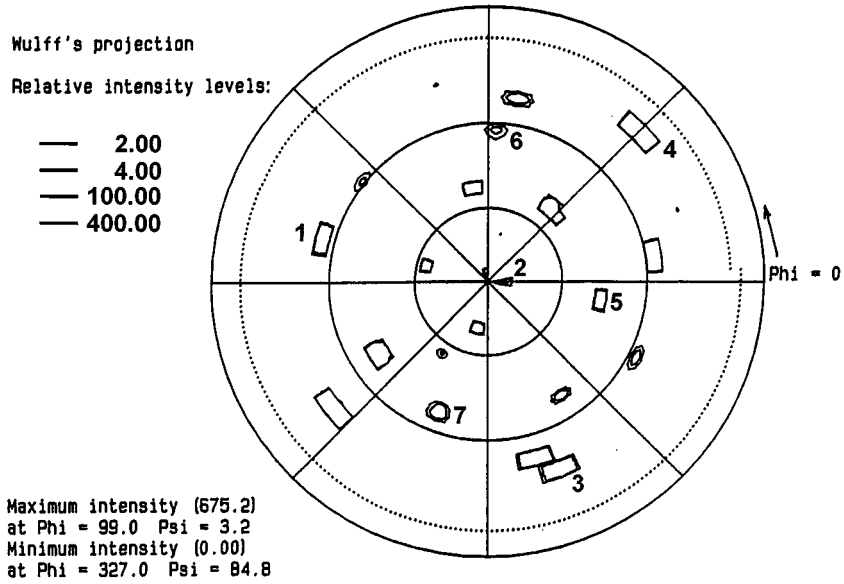


Figure 5 Pole figure plot for Ge-Fe sample undercooled by $\Delta T = 100$ K prior to nucleation. Measurement of pole angle confirms that this is a single twinned crystal.

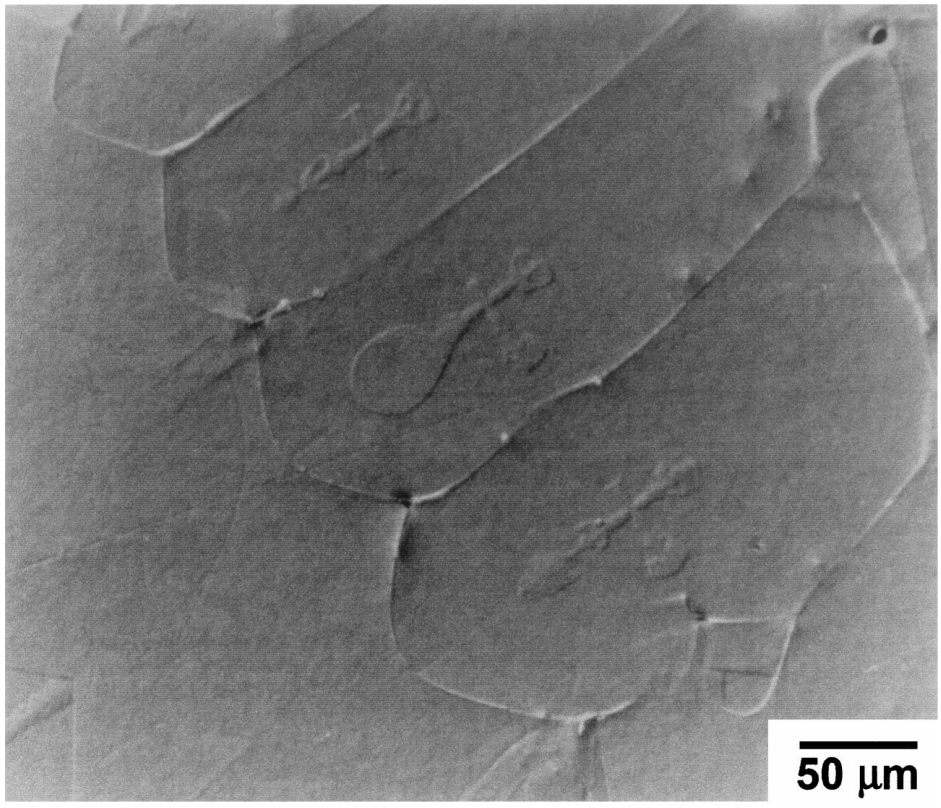


Figure 6 Optical micrograph of Ge-Fe ($\Delta T = 170$ K). The grain size is still coarse but the high density of growth twins previously observed is no longer present and the dendritic substructure has started to break up.

to continuous growth is possible as the interfacial undercooling is increased. Therefore, if such a transition from lateral to continuous growth was observed in germanium, this would be indicated by:

(1) the disappearance of growth twins from the microstructure;

(2) a sudden, but smooth, increase in the measured growth velocity-undercooling relationship, as the solid-liquid interface progressively roughens.

In Fig. 11 we have replotted our experimentally observed growth velocities in germanium together with predicted growth velocities for Ge as calculated by Li *et al.* [9]. and from the Lipton *et al.* [10] (LKT) model for continuous dendritic growth using the parameters given in Table II. For $\Delta T < 170$ K, the experimental values of growth velocity lies well below that of the predicted curve due to the large kinetic undercooling required for lateral growth. However, for undercoolings greater than 170 K the measured growth velocities start to rise to the predicted value. This was accompanied by a disappearance of growth twins in the microstructure. A similar observation was made in the Ge-Fe alloy but the transition was found to occur at a lower

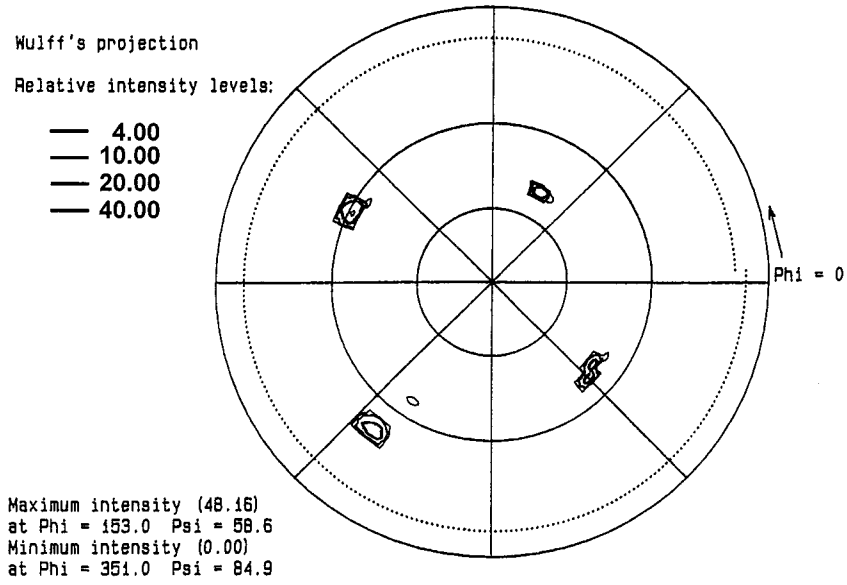


Figure 7 Pole figure plot for Ge-Fe sample undercooled by $\Delta T = 170$ K prior to nucleation. Four strong intensity {111} poles are observed.

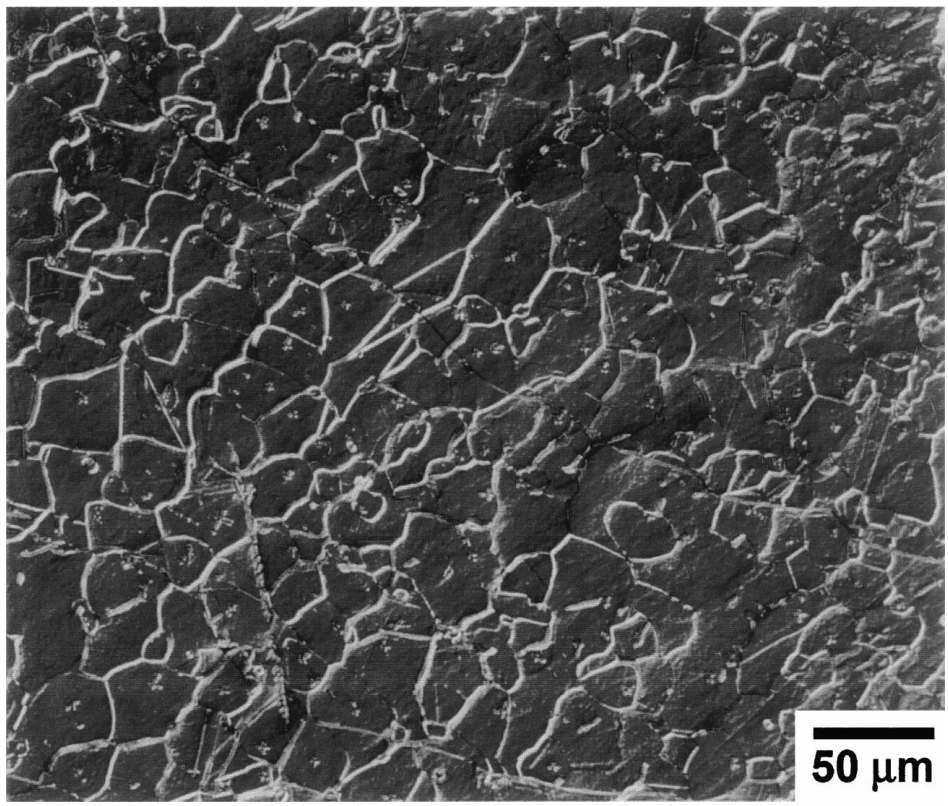


Figure 8 Optical micrograph of Ge-Fe sample undercooled by $\Delta T = 220$ K prior to nucleation. The grain size has reduced dramatically compared to that shown in Fig. 6.

TABLE II

Quantity	Symbol	Value	Units
Specific heat capacity	c_p	380.4	J kg^{-1} K^{-1}
Latent heat of fusion	H	507 000	J kg^{-1}
Thermal conductivity	κ	40	W K^{-1} m^{-1}
Density	ρ	5320	kg m^{-3}
Liquidus temperature	T_l	1210	K
Surface energy (solid-liquid)	γ	0.334	J m^{-2}
Kinetic undercooling parameter	μ	0.048	m s^{-1} K^{-1}

undercooling ($\Delta T > 150$ K). This would suggest that the presence of Fe reduces the amount of undercooling required for interface roughening.

It can be seen that with the change in growth mode from stepwise to continuous, the measured growth velocity starts to rise and tends towards the values calculated for the continuous growth of Ge. At low undercoolings, the agreement between measured and calculated data is poor. This would be expected as the twin plane re-entrant growth mechanism commonly

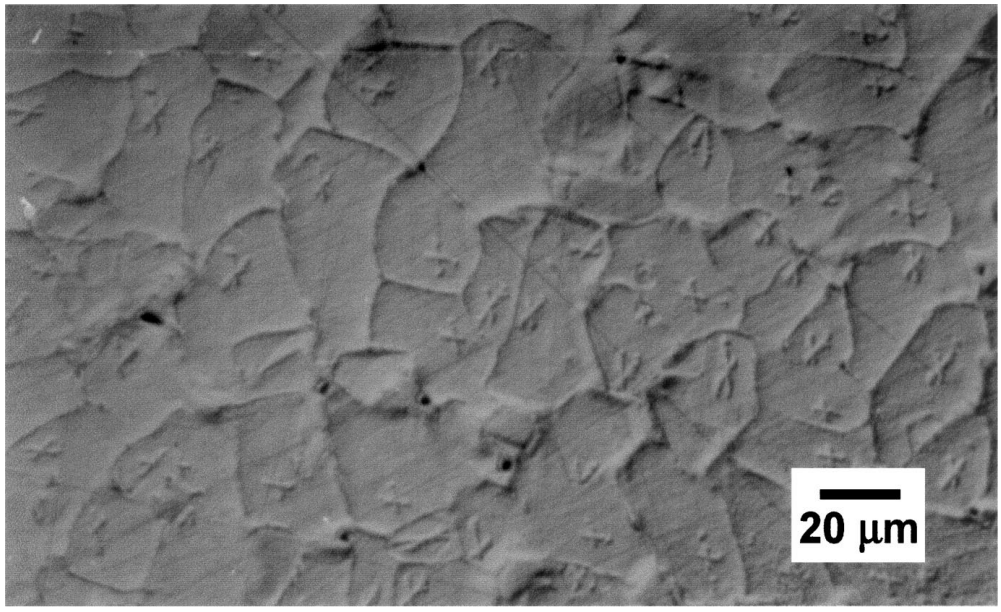


Figure 9 Optical micrograph of Ge-Fe ($\Delta T = 250$ K). Note the small cross shaped fragments at the centre of each grain.

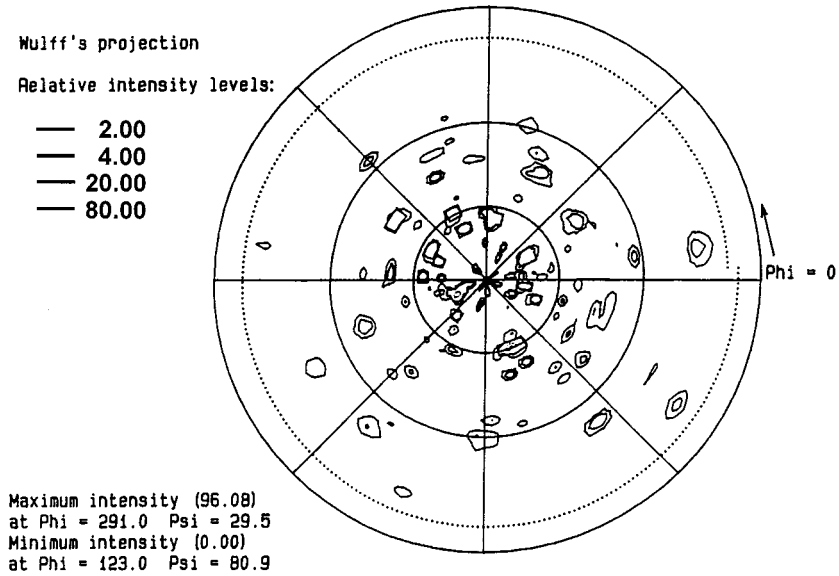


Figure 10 Pole figure plot obtained for a Ge-Fe sample undercooled by $\Delta T = 250$ K prior to nucleation. The large number of randomly distributed poles confirms that dendrite fragmentation has occurred.

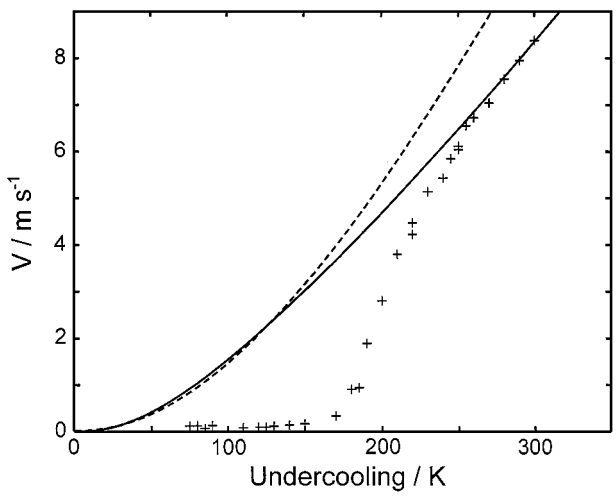


Figure 11 Measured recalescence velocity for Ge compared with the calculation of Li *et al.* [9] (dotted) and with our calculated velocity for continuous dendritic growth using the parameters given in Table I.

reported [4] would invalidate the assumptions of a parabolic dendrite, inherent in the LKT model, together with the fact that a higher kinetic undercooling is required for growth from a faceted interface. When the interface roughens at high undercoolings, there is no reason to believe that the LKT model would not describe the dendritic growth in undercooled germanium as well as it describes the growth in other pure metals showing continuous growth kinetics.

It was clear from Fig. 2 that during stepwise growth the dendrite growth velocity in Ge-Fe alloy is significantly higher than that in pure Ge. However, once continuous growth is dominant the velocities for Ge and Ge-Fe appear to converge. It would thus appear that even a very low concentration of alloying elements (100 ppm in this case) can have a dramatic effect on the growth kinetics of faceted materials, presumably by providing a roughening of the interface for atomic attachment, i.e. by providing unsaturated bonds to

allow the easier incorporation of atoms into the crystal. This effect might be termed *constitutional roughening*. Similar behaviour has been reported in dilute Ge-Sn alloys [11]. If constitutional roughening occurs, then a lower degree of kinetic roughening at the interface would be required for continuous growth to proceed, which would result in the lower critical undercooling for the change in growth mode in Ge-Fe, compared to Ge, reported here.

At the highest undercoolings achieved both Ge and Ge-Fe underwent a transition to a spontaneously grain refined microstructure, with the transition being 40 K lower in Ge-Fe. These results are consistent with the microstructural observations of previous authors in Ge-Sn [2] where the presence of 0.39 at % Sn lowered the critical undercooling for grain refinement by 50 K.

The mechanisms for such refinement have been a subject of considerable discussion since the phenomenon was first observed in Ni [12]. A number of models have been proposed for spontaneous grain refinement, with most recent models focusing of dendritic fragmentation processes, either due to a surface energy driven remelting as the dendrite size decreases [13] or due to a tip instability mechanism [14]. This later model has the advantage that it may also provide an explanation for the break in the velocity undercooling curve at ΔT^* [15]. The pole figure plots generated for the dendritic and grain refined samples (Figs 7 and 10) confirm that there has been a transition from coarse grains grown from a single dendrite with a well defined orientation to a large number of small, randomly-oriented grains.

Velocity undercooling measurements have previously been reported for Ge and its alloys with Sn and Si in a series of papers by Li and co-workers [7, 9, 16]. In their systems they observed similar trends to those reported here, in that Ge and its dilute alloys undergo a transition with increasing undercooling from faceted twinned dendritic growth, to continuous untwinned dendritic growth with grain refined equiaxed growth being observed at the highest undercoolings. Moreover they also observed that the presence of small quantities of solute could substantially enhance the growth velocity. However, there are significant differences between the growth velocities reported here and those reported by Li *et al.* particularly in respect of pure Ge. At a maximum undercooling of 300 K we determined a recalescence velocity for Ge of 8.4 m s^{-1}, compared with <0.2 m s^{-1} reported by Li *et al.* At present we are uncertain why such large discrepancies exist between the two data sets. Clearly the recalescence velocity of Ge is very sensitive to the additions of small quantities of solute, but SIMS analysis of our as-solidified samples revealed no detectable impurities ($\approx$1 ppm threshold). Systematic differences between velocity measurements made by electromagnetic levitation and fluxing techniques have previously been noted [17] in other materials, although not to the extent apparent here. However, we note that the velocities determined in this work for the growth of Ge at high undercoolings agree very closely with those calculated by Li *et al.* [9] for continuous growth in germanium. In light of the discrepancies noted between these two data sets there is a pressing case for this measurement to be made by a third laboratory.

5. Summary and conclusions

The attainment of high undercoolings, using a fluxing method, has allowed growth velocities to be measured in samples of Ge and Ge-Fe. A maximum growth velocity of 7.6 m s^{-1} was measured at $\Delta T = 250$ K in Ge-Fe and a maximum of 8.4 m s^{-1} was recorded at $\Delta T = 300$ K in pure Ge. Transitions from a stepwise to continuous growth mode were observed microstructurally in both pure Ge and Ge-Fe, accompanied by a rise in the measured growth velocity. These transitions occurred at $\Delta T > 150$ K in Ge-Fe and $\Delta T > 170$ K in pure Ge. The difference in the level of undercooling required for interfacial roughening is thought to be due to the iron impurity providing more sites for atomic attachment. The growth velocities measured in both materials in the continuous growth regime show a rise towards the values predicted by the LKT dendritic growth model. Spontaneous grain refinement was observed to occur in Ge and Ge-Fe at undercoolings of $\Delta T > 270$ K and $\Delta T > 210$ K respectively.

Acknowledgements

This work was supported by EPSRC under grant No. GR/H27250. AMM is grateful to the Royal Society for their support under the University Research Fellowship scheme.

References

1. E. BILLIG, *Proc. R. Soc.* **A229** (1955) 346.
2. G. DEVAUD and D. TURNBULL, *Acta Metall.* **35** (1987) 765.
3. C. F. LAU and H. W. KUI, *Acta Metall. Mater.* **39** (1991) 323.
4. D. R. HAMILTON and R. G. SEIDENSTICKER, *J. Appl. Phys.* **31** (1960) 1165.
5. R. S. WAGNER, *Acta Metall.* **8** (1960) 57.
6. C. F. LAU and H. W. KUI, *Acta Metall. Mater.* **41** (1993) 1999.
7. D. LI, T. VOLKMAN, K. ECKLER and D. M. HERLACH, *J. Cryst. Growth* **152** (1995) 101.
8. J. W. CAHN, *Acta Metall.* **8** (1960) 554.
9. D. LI, K. ECKLER and D. M. HERLACH, *Acta Mater.* **44** (1996) 2437.
10. J. LIPTON, W. KURZ and R. TRIVEDI, *Acta Metall.* **35** (1987) 957.
11. D. M. HERLACH, *Mater. Sci. Eng.* **A226** (1997) 348.
12. J. L. WALKER, in "The Physical Chemistry of Process Metallurgy, Part 2," Vol. 845, edited by G. R. St. Pierre (Interscience; New York, 1959).
13. M. SCHWARZ, K. KARMA, K. ECKLER and D. M. HERLACH, *Phys. Rev. Lett.* **73** (1994) 1380.
14. A. M. MULLIS and R. F. COCHRANE, *J. Appl. Phys.*, in press.
15. *Idem., ibid.* **82** (1997) 3783.
16. D. LI, K. ECKLER and D. M. HERLACH, *Eur. Phys. Lett.* **32** (1995) 223.
17. D. M. MATSON, in "Solidification 1998," edited by S. P. Marsh *et al.* (TMS, Warrendale, PA) p. 233.

Received 21 October
and accepted 16 November 1998