The microstructure of unidirectionally solidified Ag–Ge eutectic alloys

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Ag–Ge alloys containing 15 to 22 wt % Ge were unidirectionally solidified to investigate the growth conditions for fully eutectic growth (the coupled region) in the range of growth rate 1.4×10^{-4} to $1.1\,\mathrm{cm\,sec^{-1}}$ and at a temperature gradient of $200°\,\mathrm{C\,cm^{-1}}$. Primary silver was not formed in the hypereutectic Ag–Ge alloys, implying that the coupled region of Ag–Ge alloys may be different from that of the other nf–f alloy systems such as Al–Si, Fe–C, Al–Ge and Al–Fe, whose coupled regions are usually skewed towards the faceted component. It was also observed that the morphologies of primary silver, primary germanium and eutectic structure were changed with increasing growth rate. Lamellar colonies were formed prominently in the fast-grown hypereutectic alloys. As the growth rate increased the tendency for branching in massive primary germanium was so pronounced that a lamellar colony was finally formed.

1. Introduction

It has been generally recognized that the microstructure of nf–f eutectics (f = faceted, nf = non-faceted) is of irregular type, while nf–nf eutectics show regular microstructure, i.e. lamellar or rodlike. It is also known that the microstructure of nf–f eutectics can be changed in various form by an appropriate control of growth variables, such as growth rate and temperature gradient [1, 2]. Such a change of microstructure seems to arise from the anisotropic growth behaviour of the faceted phase in the nf–f eutectic system. Furthermore this phenomenon seems to cause the skewed form of the coupled region in the nf–f alloy system [3]. The exact form of the coupled regions can be readily predicted for the nf–nf alloy system. However, such a theoretical prediction is difficult for the nf–f alloy system, because there is a large discrepancy between the experimental result and the theoretical one regarding the relationship between the growth rate and the undercooling of the faceted primary phase, as well as the nf–f eutectic. nf–f irregular eutectics are characterized by a large phase spacing, large interfacial undercooling and a wide range of local spacings. It has generally been accepted that both phase spacing and undercooling in the nf–f irregular eutectics decrease with increasing temperature gradient [4, 5].

Jackson and Hunt [6] proposed a relationship between the undercooling and the growth rate for nf–nf regular eutectics, and so far their relationship has been found experimentally to predict the behaviour of regular eutectics fairly well. However, such a relationship for nf–f irregular eutectics has not yet been proposed. Recently, Fisher and Kurz [4] suggested a new theory based on the non-extremum growth model, in which they proposed that nf–f eutectics could be described by the relation $\lambda^2 R = kG^{-m}$, where λ is the phase spacing and k, m are constants. This relation implies that the microstructure of nf–f eutectic may be controlled by such growth variables. The change in microstructure resulting from the variation of growth variables and dependence on the mechanical properties were extensively studied in some nf–f eutectic systems, for commercially important alloy systems such as Al–Si [7] and Fe–C [8]. As the microstructure of the Ag–Ge eutectic system consists of a good conductor phase (silver solid solution) and a semiconductor phase (germanium), it is expected that the alloy might have applications as an electrical material such as an anisotropic conductor [9], rather than a mechanical application. For such an application, the relationship between the microstructure and the growth condition for this system should be elucidated.

The present work is aimed at investigating the dependence of the microstructure of the Ag–Ge eutectic alloy system on the growth conditions, by varying the growth rate and the alloying composition. The growth condition for fully eutectic structure without the formation of a primary phase (the coupled region), and the dependence of the microstructure of the primary phases as well as the eutectic on growth rate will also be examined.

2. Experimental procedure

Ag–Ge alloys containing 15 to 22 wt % Ge were prepared from high-purity 99.99% Ag and 99.999% Ge. All alloys were prepared by first melting the pure metal in a vacuum (10^{-2} torr) in sealed transparent silica tubes of 6 mm internal diameter, producing a rod of 6 mm diameter and 25 to 30 mm long. Melting was conducted in a gas burner using a propane–oxygen mixture, in which the melting temperature was controlled at 1000 to 1050° C.

The alloy specimens were then vacuum-sealed once again in the silica tube, and subjected to unidirectional solidification in a Bridgeman type vertical furnace.

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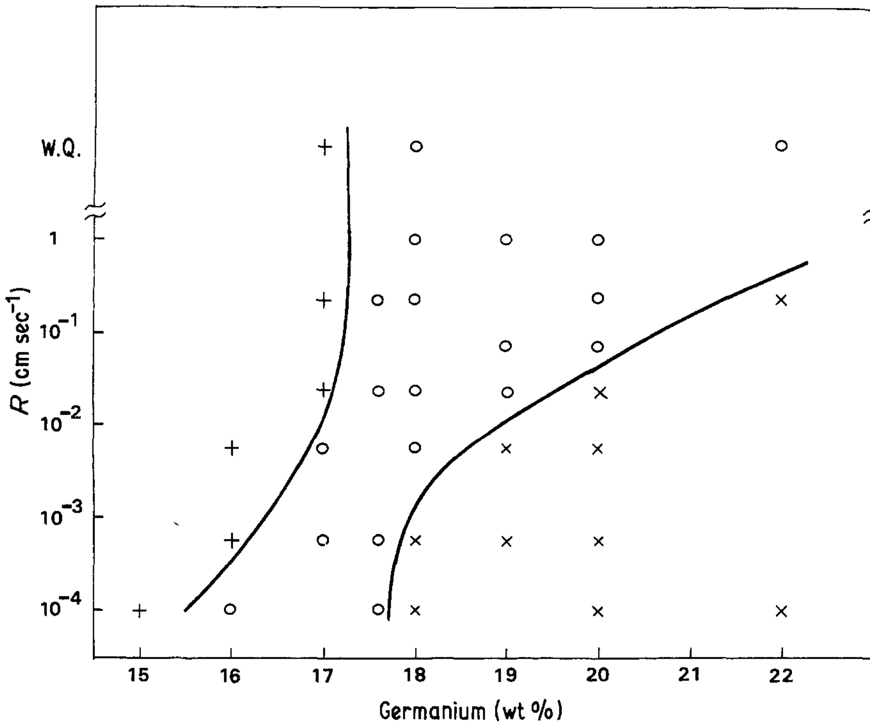


Figure 1 The coupled region of the Ag–Ge eutectic system as a function of alloy composition and growth rate. W.Q. means water-quenched. (+) Primary α, (○) eutectic, (×) primary germanium.

Prior to unidirectional solidification, the alloy specimens were held for 1 h in the melting zone of the furnace for homogenization of alloying elements. Traction rates which approximated to the growth rates were controlled within the range 1.4×10^{-4} to $1.1\,cm\,sec^{-1}$ by a reduced motor with a stepped driving shaft. By circulating cooling water in a copper pipe below the heating element and keeping the highest temperature in the furnace at 1000° C, the measured temperature gradient within the specimen was $200°\,C\,cm^{-1}$ for a traction rate of $2.2 \times 10^{-2}\,cm\,sec^{-1}$. While this temperature gradient is changeable for different traction rates, the effect of temperature gradient is of little significance in controlling the coupled region in the present work, at least in the range of high growth rates. The specimen in the furnace was attached to a stainless steel rod (4 mm diameter), which was suspended from the shaft of the motor by a thin Fe–Cr wire (0.14 mm diameter). The stainless steel rod was used in order to maintain vertical alignment of the specimen and to allow smooth withdrawal during unidirectional solidification. After the solidification, each 3 mm from the top and bottom of the solidified specimen were discarded, and the remaining portion was cut with a jeweller's saw into transverse and longitudinal sections. The achievement of steady-state solidification near the middle of the rod was confirmed by microstructural examination of the entire length of solidified rod.

The initial and final transient regions seemed to be ~ 1 mm in length. Transverse and longitudinal sections were prepared for optical microscopy by conventional metallography and the microstructure was examined unetched.

3. Results and discussion

3.1. The coupled region

The range of composition as a function of growth rate within which primary silver, primary germanium and fully eutectic structure can be obtained is indicated in Fig. 1. Neither primary silver nor primary germanium was observed at any growth rates in alloys of 17.6 wt % Ge, which Maucher [10] reported as the eutectic composition. Primary silver was formed at higher growth rates for compositions below 17.6 wt % Ge, while at lower growth rates for the same composition range the eutectic structure was formed.

Primary germanium was formed at lower growth rates for compositions > 17.6 wt % Ge, while eutectic structure was formed at higher growth rates for the same composition range. Since primary silver and germanium were observed in hypo-eutectic and hyper-eutectic alloys, respectively, the coupled region of the Ag–Ge system may be classified as within the nf–nf system in this sense. However, in hypo-eutectic nf–nf alloy solidified at high growth rates the primary phases are formed at lower growth rates, while at higher growth rates eutectic structure is formed. This was not, however, the case for the Ag–Ge system.

It is known that the coupled region of the nf–f system is skewed toward the faceted component. Thus, the non-faceted primary phase can be observed in a hyper-eutectic alloy. For example, primary aluminium is formed in fast-growing hyper-eutectic Al–Si alloy, while primary silicon or eutectic structure are formed at low growth rates [11]. However, in hyper-eutectic Ag–Ge alloys primary silver was not observed even at growth rates exceeding $1.1\,cm\,sec^{-1}$. Such behaviour was supported by the finding that primary silver was not observed in the quenched hypereutectic alloys. Thus it may be cautiously concluded that the coupled region of the Ag–Ge system is somewhat different from that of the other nf–f systems such as Al–Si, Fe–C [12], Al–Ge [13] and Al–Fe [14], in that the non-faceted primary phase is not formed in hyper-eutectic alloys.

Some workers [15, 16] have predicted the form of

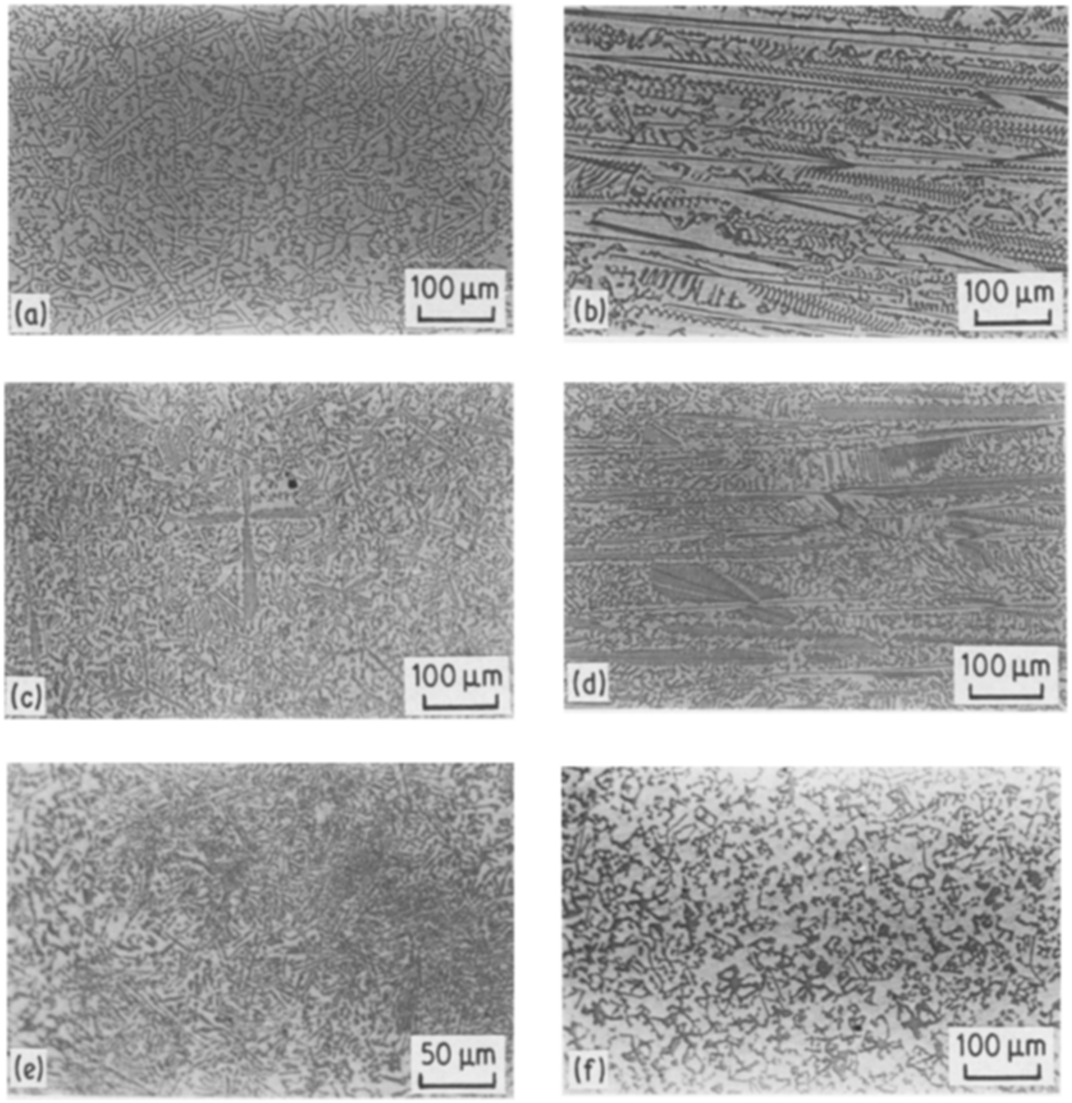


Figure 2 Microstructure of Ag–Ge eutectic alloy (17.6 wt % Ge) at various growth rates: (a, b) $R = 1.4 \times 10^{-4}\,\mathrm{cm\,sec^{-1}}$, $G = 200°\,\mathrm{C\,cm^{-1}}$; (c, d) $R = 5.6 \times 10^{-4}\,\mathrm{cm\,sec^{-1}}$, $G = 200°\,\mathrm{C\,cm^{-1}}$; (e) $R = 2.2 \times 10^{-1}\,\mathrm{cm\,sec^{-1}}$, $G = 200°\,\mathrm{C\,cm^{-1}}$; (f) $R = 1.4 \times 10^{-4}\,\mathrm{cm\,sec^{-1}}$, $G = 60°\,\mathrm{C\,cm^{-1}}$. (a), (c), (f) are transverse and (b), (d), (e) are longitudinal sections relative to the growth direction.

the coupled region. Burden and Hunt [16] showed, using a competitive growth model, that the coupled region could be expressed in the following equation: $\Delta C = AGD/R + BR^{1/2}$, where A and B are constants, D is the diffusion coefficient, ΔC is the composition range within which a fully eutectic structure can be obtained, G is the temperature gradient and R the growth rate.

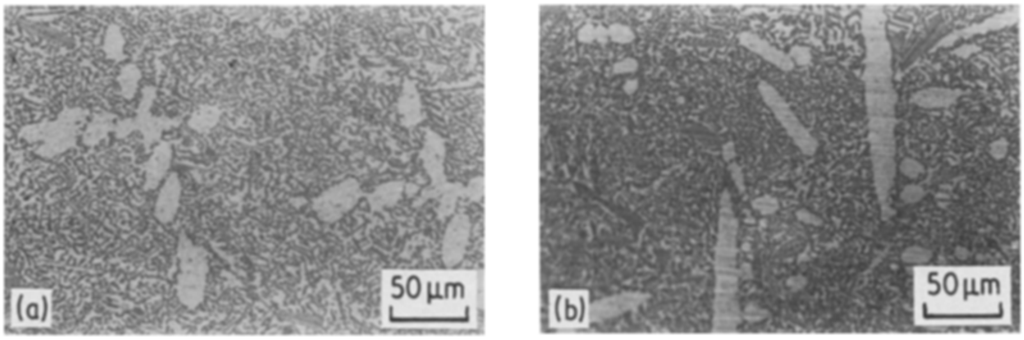
The large discrepancy between the experimental result and the value calculated with this equation causes difficulties in predicting the coupled region of the nf–f alloy system. The work of Fisher and Kurz [3] has shown that the Burden and Hunt's dendrite analysis [17] does not give even a rough approximation to the relationship between the growth rate and the undercooling for the faceted phase, though it gives a reasonable fit for the non-faceted phase. Accordingly Fisher and Kurz [3] tried to elucidate the undercooling–growth rate relationship of the primary silicon phase in the Al–Si system using another equation which can be applied to the platelet morphology; the prediction for the coupled region of the Al–Si system then approached more closely the experimental results. However, in the present work such a comparison was not possible for the Ag–Ge system due to the lack of some important thermodynamic data.

The above equation implies that at high growth rates the $R^{1/2}$ term predominates and the effect of the temperature gradient may be negligible, so that the coupled region is approximately proportional to $R^{1/2}$. For such a reason the effect of temperature gradient on the form of the coupled region might be considered to be negligible in the present work, because the growth rates employed were large. However, the coupled region as shown in Fig. 1 was believed to be available, strictly speaking, only at the temperature gradient of $200°\,\mathrm{C\,cm^{-1}}$, because the effect of temperature gradient should be taken into account in the range of low growth rates (1.4×10^{-4} to $5.6 \times 10^{-4}\,\mathrm{cm\,sec^{-1}}$).

3.2. Microstructural change with increasing growth rate

3.2.1. Eutectic structure

Fig. 2 shows micrographs of the Ag–Ge eutectic alloys obtained at various growth rates. The growth rates were varied within the range of 1.4×10^{-4} to $2.2 \times 10^{-1}\,\mathrm{cm\,sec^{-1}}$, while the temperature gradient



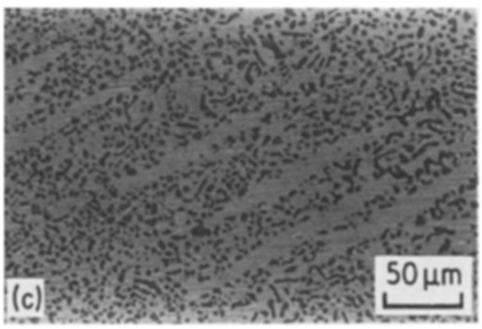


Figure 3 Morphologies of primary silver at various growth rates (17 wt % Ge): (a) $R = 2.4 \times 10^{-2}$ cm sec^{-1}, (b) $R = 2.2 \times 10^{-1}$ cm sec^{-1}, (c) water-quenched.

was fixed at 200° C cm^{-1} for most specimens. Some specimens were grown also at a temperature gradient of 60° C cm^{-1} in order to investigate the influence of temperature gradient on the microstructural change.

The average phase spacing decreases and the microstructure changes gradually with increasing growth rate. At $R = 1.4 \times 10^{-4}$ cm sec^{-1} the eutectic alloy grows in the form of a "quasi-regular" structure (Fig. 2a). "Featherlike" morphology (Fig. 2c) was frequently observed at $R = 5.6 \times 10^{-4}$ cm sec^{-1}. This morphology is considered to be a result of the branching of the germanium particle with increasing growth rate [18]. In alloys grown at 2.2×10^{-1} cm sec^{-1} a mixed structure of irregular fibres and irregular flakes was observed as shown in Fig. 2e. The average phase spacing was 10.5 μm in the irregular fibre structure, while that of the irregular flake structure was 3 μm. However, in a water-quenched specimen the microstructure was only of irregular flake type. Fig. 2f shows the microstructure at a growth rate of 1.4×10^{-4} cm sec^{-1} and a temperature gradient of 60° C cm^{-1}. In comparison with Fig. 2a, the microstructure is of "starred rod" type.

From this it can be deduced that increasing the temperature gradient results in a branching of germanium particles and thus a microstructural change occurs. It was found that the phase spacing decreased slightly with increasing temperature gradient, which corresponds qualitatively to Fisher and Kurz's relation [4] that is represented by $\lambda^2 R = kG^{-m}$.

They have suggested that the branching of the faceted phase occurs as the temperature gradient increases, leading to a decrease of phase spacing. However, an examination of the microstructure shows that the influence of temperature gradient on the microstructural change seems to be negligible at growth rates higher than 5.6×10^{-4} cm sec^{-1}. Thus, it is concluded that the microstructural change is not strongly sensitive to the variation of temperature gradient at substantially high growth rates.

Generally, the anisotropic growth behaviour of faceted phases seems to make it difficult or impossible to form a high degree of directionality in the microstructural feature of the nf–f eutectic, even if a unidirectional solidification technique is adopted. However, in the alloys grown at low rates (Fig. 2b, d) they showed some directionality of the microstructure though its extent was limited. On the other hand, the microstructure in alloys grown at higher rates (2.8×10^{-3} cm sec^{-1}) shows no directionality. This might be explained as follows: the cooling rate in the specimen becomes lower compared with the traction rate of the specimen as the traction rate of the specimen in the furnace increases. Thus the temperature of the specimen still remains high although the specimen has just passed through the low-temperature zone in the furnace. In such a situation the heat transfer in the specimen itself is not only downward, but also radial or in other directions. This three-dimensional heat transfer in the specimen is considered to cause the non-directional growth in the specimens solidified at high growth rates.

3.2.2. *Primary silver*

A 17 wt % Ge alloy was examined to investigate the morphological transition of a primary silver with an increasing growth rate. Microstructural examination showed that a fully eutectic structure was formed at low growth rate, whereas primary silver was formed at higher growth rates (2.4×10^{-2} cm sec^{-1}), as indicated in Fig. 1.

Primary silver was easily identified by its dendritic morphology in alloys grown at $R = 2.4 \times 10^{-2}$ cm sec^{-1} (Fig. 3a). The dendritic morphology was destroyed by further increase in growth rate (Fig. 3b), and cylindrical morphology was revealed in the water-quenched specimen (Fig. 3c), and the eutectic germanium was of fine spherical morphology.

Ojha and Ramachandrarao [19] have reported that primary silver undergoes morphological transitions, dendritic → cylindrical → spherical, in undercooled Ag–Ge hypo-eutectic alloys as the degree of undercooling increases.

They explained this phenomenon on the basis of remelting of dendrite arms on recoalescence. In the

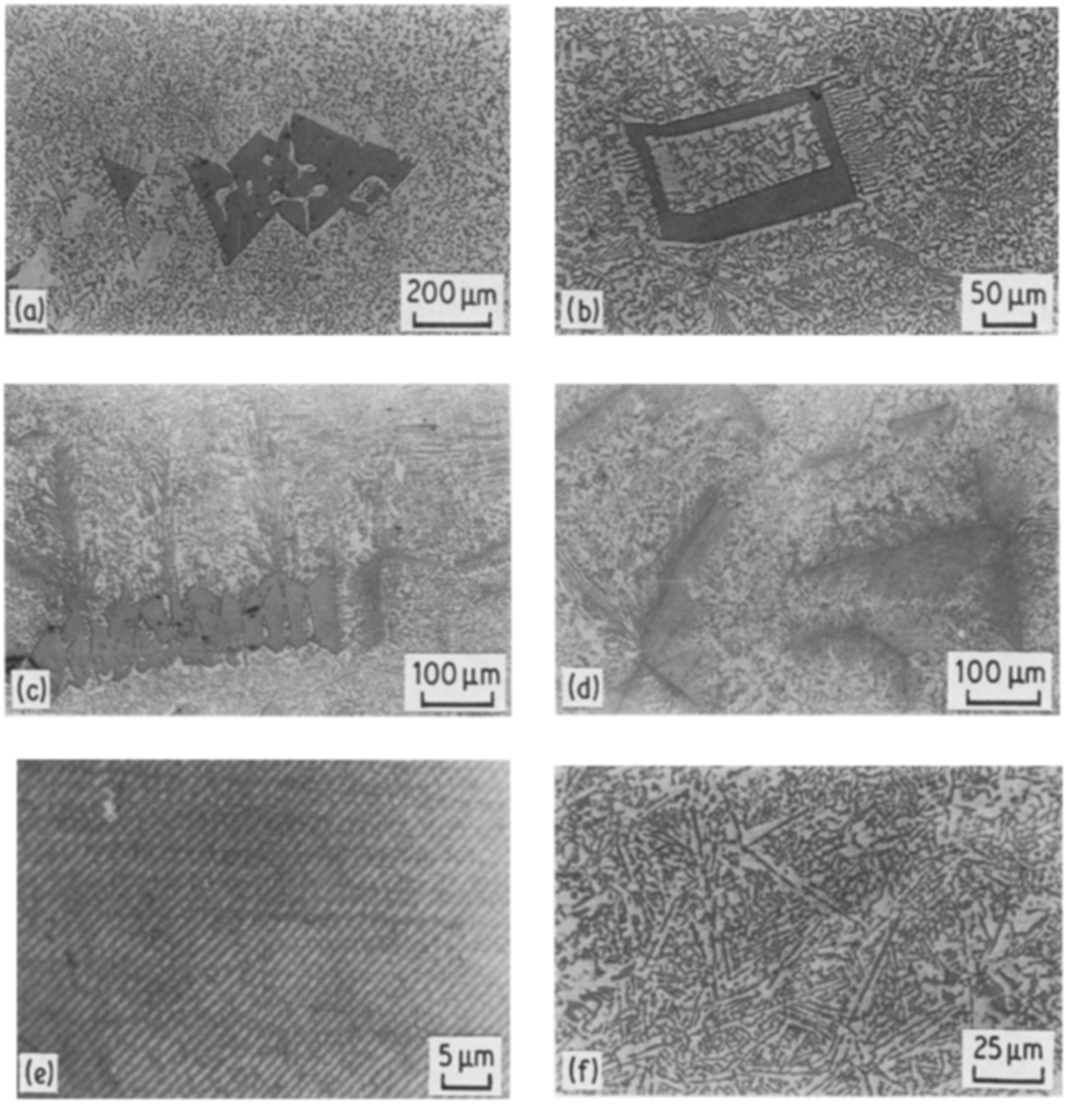


Figure 4 Branching of primary germanium with increasing growth rate (20 wt % Ge, $G = 200° \mathrm{C\,cm^{-1}}$): (a) $R = 1.4 \times 10^{-4} \mathrm{cm\,sec^{-1}}$, (b) $5.6 \times 10^{-4} \mathrm{cm\,sec^{-1}}$, (c) $5.6 \times 10^{-3} \mathrm{cm\,sec^{-1}}$, (d, e) $7.5 \times 10^{-2} \mathrm{cm\,sec^{-1}}$, (f) $1.1 \mathrm{cm\,sec^{-1}}$.

present work, cylindrical morphology was observed when the growth rate was further increased by quenching the specimen. This observation corresponds to Ojha and Ramachandrarao's results [19] in view of the high undercooling caused by a high growth rate. However, the degree of thermal undercooling could not be determined in the quenched specimen, since thermal analysis was not undertaken in the present work.

3.2.3. Primary germanium

Primary germanium is characterized by its massive, angular form with non-dendritic morphology as well as its anisotropic growth behaviour.

From the examination of slow-growing alloys the mould surface is shown to be the preferred site for the nucleation of primary germanium, in contrast with the case for primary silver. Fig. 4 shows the morphological change of primary germanium in Ag–20 wt % Ge alloys grown at various growth rates from 1.4×10^{-4} to $1.1 \mathrm{cm\,sec^{-1}}$.

In alloys grown at $R = 1.4 \times 10^{-4} \mathrm{cm\,sec^{-1}}$, massive primary germanium was observed (Fig. 4a), and with increasing growth rate the tendency for branching in massive germanium was very pronounced; lamellar colonies evenly distributed all around the specimen were frequently observed in alloys grown at $R = 7.5 \times 10^{-2} \mathrm{cm\,sec^{-1}}$ (Fig. 4b to d), and a lamellar colony observed at higher magnification (Fig. 4e) showed the formation of a perfect lamellar structure. In the lamellar colony the volume occupied by germanium is approximately equal to that occupied by silver. The proportion of lamellar colonies in the total area was slightly retarded by the further increase of growth rate.

Billig [20] and Billig and Holmes [21] reported that germanium grown in the $\langle 2\,1\,1 \rangle$ direction from seeded supercooled melts contained a thin lamellar colony due to branching in the $\langle 2\,1\,1 \rangle$ direction, and the germanium crystal was of $(1\,1\,1)$ twinned structure. Later, it was shown theoretically by Wagner [22] and Hamilton and Seidensticker [23] that at least two twin planes should be present in the germanium crystal for continued propagation in the $\langle 2\,1\,1 \rangle$ direction.

According to Lemaignan and Malmejac [18], germanium grew in the $\langle 1\,0\,0 \rangle$ direction at low growth rates, and in the $\langle 2\,1\,1 \rangle$ direction at growth rates higher than a certain level. Also they showed that germanium crystals in Ag–Ge eutectic alloys were always of multiple twinned structure, which was of

(2 1 0) type at lower growth rates and (1 1 1) type at higher growth rates.

From the findings described above, it is concluded that in Ag–Ge alloys grown at high growth rates, primary germanium has at least two (1 1 1) twin planes and grows in the ⟨2 1 1⟩ direction. Accordingly it is concluded that the branching of primary germanium in the ⟨2 1 1⟩ direction should occur in fast-grown Ag–Ge alloys. However, these observations are not enough to explain the continuous increase of branching, because at growth rates higher than a certain level germanium crystals grow in the ⟨2 1 1⟩ direction, having a twinned structure of the (1 1 1) type as mentioned previously. Further study on the relationship between the crystallography of germanium and the growth rate is required to clarify the mechanism involved.

In the present work the lamellar colony is considered as another form of eutectic structure, because the branching of eutectic germanium particles is also frequently observed in metal–germanium systems. Therefore, the structure where a massive germanium particle was not formed is regarded as the eutectic structure, regardless of the presence of the lamellar colony.

4. Summary and conclusions

1. The coupled region of the Ag–Ge eutectic system is somewhat different from those of other nf–f eutectic systems, whose coupled regions are characterized by a skewed form leaning towards the faceted component. Thus primary germanium was not formed in hyper-eutectic alloys at fairly high growth rates, contrasting with the other nf–f systems where a faceted primary phase is formed in fast-growing hyper-eutectic alloys.

2. The eutectic structure changed with increasing growth rate: "quasi-regular" structure at low growth rates, a mixed structure of irregular fibres and irregular flakes at intermediate growth rates, and irregular flakes in a water-quenched specimen. The eutectic structure seemed to be sensitive to the variation of the temperature gradient at low growth rates.

3. The lamellar colony observed in the fast-growing hyper-eutectic alloys originated from massive primary germanium, whose branching was promoted by an increase of the growth rate. The phenomenon of branching in primary germanium seemed to be closely related with crystallographic changes in the germanium crystal with increasing growth rate.

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