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Thermodynamic criterion of separated eutectic phenomena

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About 26 kinds of simple and complex binary eutectics were frozen directionally under the condition of electromagnetic stirring. It was found that anomalous eutectics including most metals/non-metals and some metal/intermetallic eutectics, can be separated on macroscopic scale by flow caused by electromagnetic stirring. Moreover, the eutectics in which one of their component phases possess an entropy of solution over 23 J mol^{-1} K^{-1}, showed notable separation. In addition, process factors also affect the formation of a separated eutectic.

1. Introduction

The eutectic growth is often considered to be similar to that of pure metals, because it takes place at one fixed temperature below the equilibrium temperature. Thus, there is no intrinsic reason for the occurrence of macroscopic segregation of the constituent elements. However, there are several reports on separated eutectic phenomena, in which a model of flow is proposed to explain the formative mechanism of these phenomena [1,2]. Recently, it was also found that separated eutectic phenomena are connected by their thermodynamic data. Some of them may be separated on a macroscopic scale, while the others are impossible. This suggests the possibility of making *in situ* surface composites.

2. Experimental procedure

The alloys were prepared from pure Al, Ni, Si, Pb, Sb, Mn, Fe, Bi, Mg, Zn, Cu, Cd, Fe, G, Co, etc. The compositions of the mother alloys were ascertained by hot chemical analysis.

The experimental apparatus was composed of a vertical Bridgman device and a electromagnetic stirrer [2]. The stirrer, made up of two-pole binary phase coils, induces a rotated flow in the melt with a rotation rate up to 20 r.p.s. for Al–Si eutectic, which is controlled by adjusting the voltage imposed on it. The rotation rate is obtained by stroboscopic measurement of the revolution rate of the axis of a ceramic paddle immersed in the melt. The unidirectional solidification is performed by lowering the crucible from the furnace at a speed of 0.05–0.15 mh^{-1}. The procedure is as follows: (1) approximately 0.75 kg alloy was weighed into an alumina crucible (0.01 mID × 0.21 m high); (2) the alloy was melted in the apparatus by a heating element; (3) the melt was stirred for about 30 min to homogenize it. (4) the draw-down speed and rotation rate were set and the cooling water flow was turned on through the bottom block; (5) samples were prepared from the specimens, observing macro- and microstructures.

3. Results and analyses

Typical microstructures of separated eutectics are shown in Fig. 1. It is seen that two-component phases of eutectics, formerly growing cooperatively, are separated to form hypoeutectic structures in the inner area, while free faceted phases, Sb, Bi, Si, Zn, etc., accumulated on the periphery of the specimens. Numerous very fine faceted particles adhered closely to the specimens. This phenomenon differs from the individual growth of each phase regardless of the presence of the second phase [3]. For the anomalous eutectic, the solid/liquid interface is usually considered to be non-isothermal where the faceted phase protrudes into the common interface, causing it to grow due to its interface boundary energy anisotropy, thermal anisotropy as well as growth anisotropy. These can promote overgrowth of the faceting phase in an anomalous structure by the non-faceting phase at a frequency that depends on the growth velocity [4]. For this reason, the leading faceted phases, generally non-metal or intermetallic phases, are broken and carried to the crucible wall to form the faceted

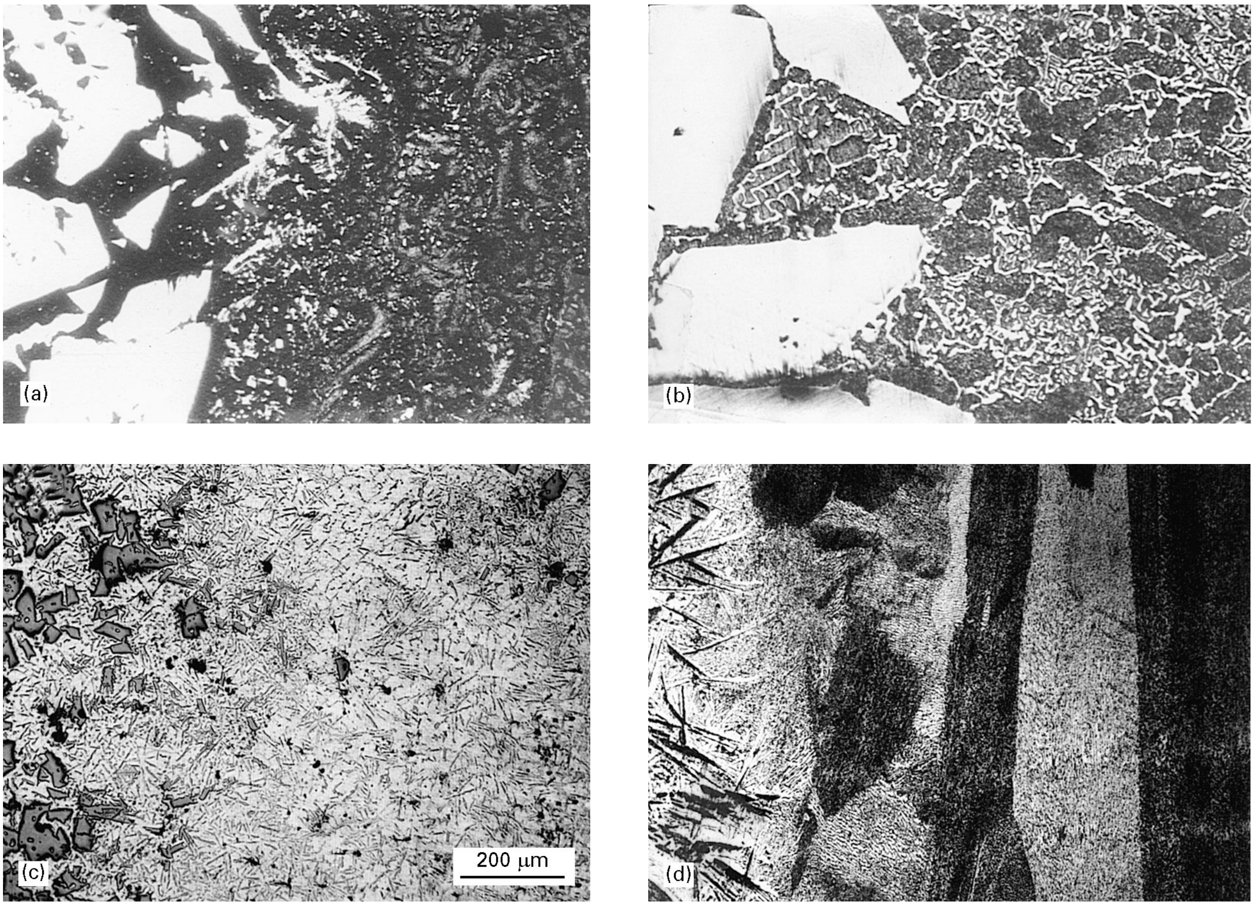

Figure 1 Microstructures of a separated eutectic: (a) Pb–Sb system, (b) Pb_2Bi–Bi system, (c) Al–Si System, (d) Sn–Zn system.

TABLE I Separated eutectic results versus entropies of solution, atomic fractions and crystal structures

Eutectic systems A	Atomic fractions B (%)	Crystal structures		Separated phases	ΔS_A ($J\,mol^{-1}\,K^{-1}$)	ΔS_B ($J\,mol^{-1}\,K^{-1}$)	Growth rates ($m\,h^{-1}$)	Rev rates ($rev\,s^{-1}$)
		A	B					
Zn–Mg_2Zn_{11}	53.4	h c p	cu				0.08	8.3
Al–Al_2Cu	49.7	f c c	b c t		12.9	15.1	0.06	10.0
Cd–Bi	43.5	h c p	rhom	Bi	16.7	26.2	0.06	10.3
Sn–Pb	35.2	f c c	f c c				0.06	10.3
Sn–Bi	35.1	f c c	rhom	Bi	9.0	24.9	0.06	10.3
Zn–Al	30.9	h c p	f c c				0.06	14.3
Sn–Cd	29.4	f c c	h c p	Bi			0.06	10.3
Pb_2Bi–Bi	27.0	h c p	rhom		10.3	24.3	0.08	10.3
Pb–Cd	23.5	f c c	h c p		8.9	22.7	0.06	10.3
Cd–Zn	23.1	h c p	h c p		11.2	20.1	0.06	10.3
Pb–Mg_2Pb	18.2	f c c	ortho		8.4	29.3	0.08	5.0
Sn–Mg_2Sn	15.0	f c c	f c c	Mg_2Sn	14.6	43.0	0.08	6.7
Pb–Sb	13.1	f c c	rhom	Sb	8.5	33.8	0.08	10.3
Sn–Zn	12.5	f c c	h c p	Zn	15.4	31.8	0.08	10.3
Al–Si	11.0	f c c	f c c	Si			0.10	12.7
Al–$NiAl_3$	10.8	f c c	ord ortho	$NiAl_3$			0.06	14.3
Fe–C	8.8	f c c	hex	C			0.06	5.8
Cd–$CuCd_3$	7.8	h c p	comp hex	$CuCd_3$			0.08	7.5
Al–Al_6Mn	7.0	f c c	ortho	Al_6Mn			0.06	14.3
Al–Al_3Fe	4.0	f c c	ord f c c	Al_3Fe			0.1	14.3
Zn–Sb_2Zn_3	3.7	h c p		Sb_2Zn_3			0.08	10.3
Al–Al_9Co_2	2.5	f c c	mono	Al_9Co_2			0.08	15.0
Sn–Sn_2Co	2.4	f c c		Sn_2Co			0.08	6.7
Sn–Al	2.2	f c c	f c c	Al	13.9	51.2	0.08	10.3
Sn–Cu_6Sn_5	1.3	f c c	hex	Cu_6Sn_5			0.08	6.7
Al–SbAl	0.5	f c c	cu	SbAl			0.08	14.3

phase-rich layer on the periphery of a specimen by forced flow, while normal eutectics only coarsen and degenerate the lamellar spacing no matter how large the flow.

A similar segregation phenomenon is also confirmed when the melt flow is caused by mechanical stirring instead of electromagnetic force.

Table I shows some thermodynamic data and experimental results on separated eutectics. It is obvious that a separated eutectic is connected with the thermodynamic data, that is, the anomalous eutectics in which one component phase possesses a solution entropy over 23 J mol^{-1} K^{-1} show notable separation behaviour while the normal eutectics are impossible to separate, whether or not they are simple or complex eutectic alloys.

In addition to the thermodynamics values, it was also found that the thickness of the separated eutectic increases with increasing rotation rate and decreasing growth rate, as shown in Fig. 2. Fig. 3 shows that the lateral distribution of silicon content decreases along the radial direction with increasing rotation rate and decreasing growth rate. This coincides with the results of increasing lamellar spacing due to velocity gradient increase along the radius [5].

Fig. 4 shows the macrostructures of various shaped specimens. For a square section crucible, the enriched layer is not even due to different flow conditions, being thicker facing upstream and towards the convex point of the inner surface (Fig. 4a). Similarly, the enriched layer is also non-uniform at different heights and radii for a complex shape crucible (Fig. 4b).

In addition, the separated eutectic phenomena also take place in hypoeutectic and ternary eutectic alloys. In particular, the ternary eutectic Al–27 wt % Cu–5.25 wt % Si can be separated, although the binary eutectic Al–33.2 wt % Cu is a normal eutectic.

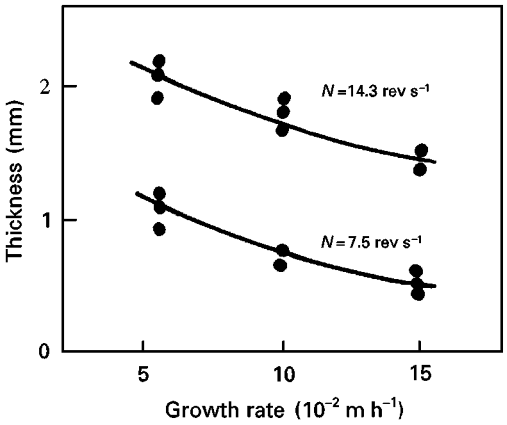

Figure 2 Enriched layer thickness versus solidification.

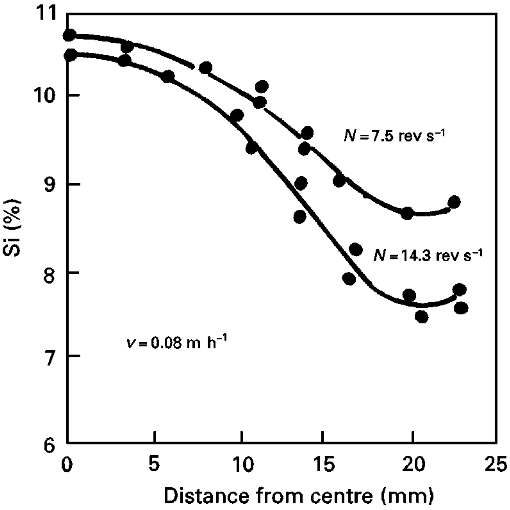

Figure 3 Distribution of silicon content in the matrix of the specimen.

4. Discussion

In order to check whether the non-equilibrium solidification condition is realized due to the melt flow, the solid–liquid interface temperature was carefully measured. Repeated measurements, using 0.1 mm diameter chromel–alumel thermocouples, show that the solid–liquid interface temperature for the non-stirred and stirred cases is almost the same within 1 °C. Thus the interface is neither supercooled nor undercooled to an amount sufficient to result in the noted non-equilibrium solidification, which causes individual growth of the eutectic phase regardless of the presence of the second phase. Based on the above result, the eutectic separation may be considered to take place under a near-equilibrium and to have something to do with its growth mechanism.

As shown above, the solid–liquid interface is usually uneven for some eutectics due to its anisotropy, so the separated eutectic is relevant to the property of the eutectic component, as is the eutectic microstructure. Before discussing the formative mechanism of a separated eutectic, let us first recall the classification of eutectics.

The solution entropy is found to be the key thermodynamic factor dominating the eutectic microstructure. Normal microstructures (lamellar and rod-like) exist when the entropy of a solution is less than 23 J mol^{-1} K^{-1}, while anomalous eutectics, such as broken lamellar, irregular flake, quasi-regular, fibrous and other complex regular microstructures, take place at higher values of solution entropy. Eutectic microstructures are broadly divided into normal and anomalous groups in the analysis of Croker *et al.* [6]. Usually the normal eutectics are frequently described as non-faceted (NF/NF), whereas anomalous eutectics are called faceted/non-faceted (F/NF). At any given rate of growth, the volume fraction of the phase with the higher solution entropy enables one to determine the particular microstructure that will arise in either of the groups. Each type of microstructure occupies a characteristic region in the V_f versus ΔS plot, as shown in Fig. 5.

Similarly, the solution entropy is also valid and useful as a criterion of a separated eutectic. The separated eutectic is sensitive to the growth mechanism of

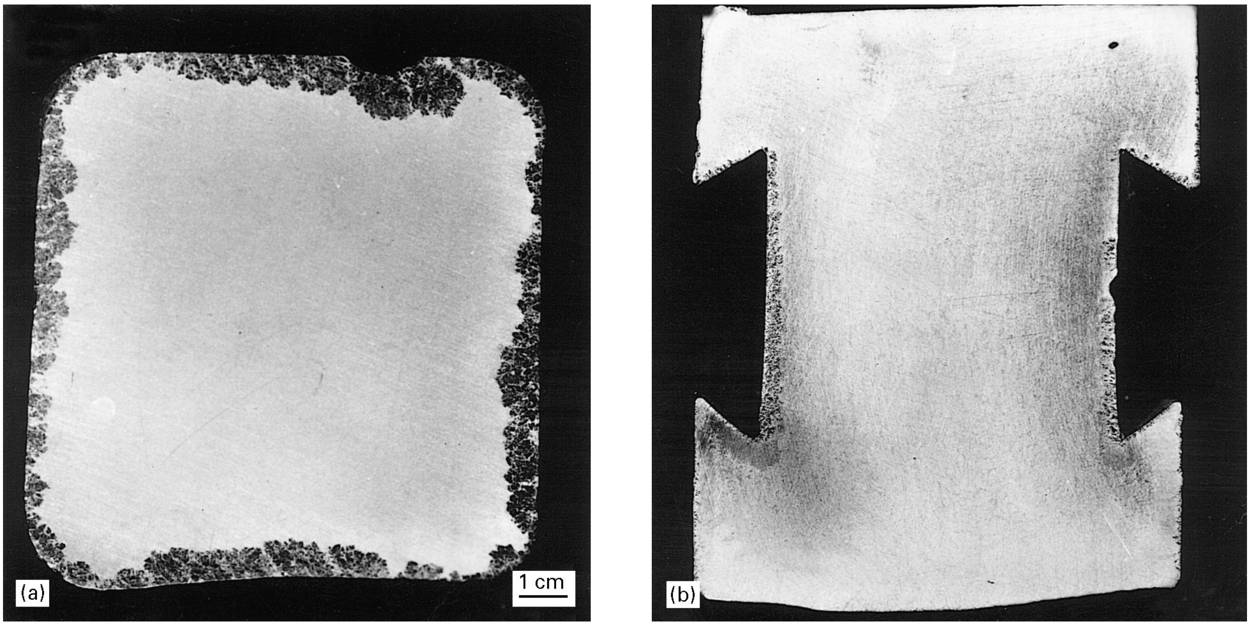

Figure 4 Macrostructures of a separated eutectic in the Al–Si eutectic: (a) square crucible, (b) crucible with trenches.

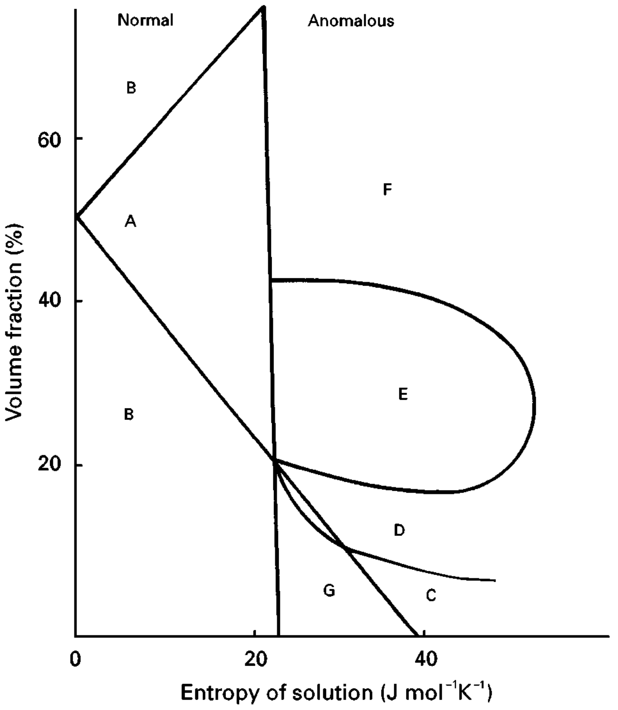

Figure 5 Classification of eutectic microstructures in terms of volume fraction and solution entropy for a growth velocity (A) normal lamellar, (B) normal rod, (C) anomalous broken lamellar, (D) anomalous irregular flake, (E) anomalous complex regular, (F) anomalous quasi-regular, (G) anomalous fibrous structure (after [6]).

faceted phases, the temperature gradient in the liquid, alloy composition, anisotropy properties of the phases and small quantities of impurities. As a result, it is not difficult to understand why a separated eutectic can only produce an anomalous eutectic.

The volume fraction also plays an important part in the formation of a separated eutectic. For those anomalous eutectics of low volume fraction, namely less than $1/2\pi$, there is large discontinuous lamellar spacing, which is sensitive to forced flow and easy to break to form a separated eutectic.

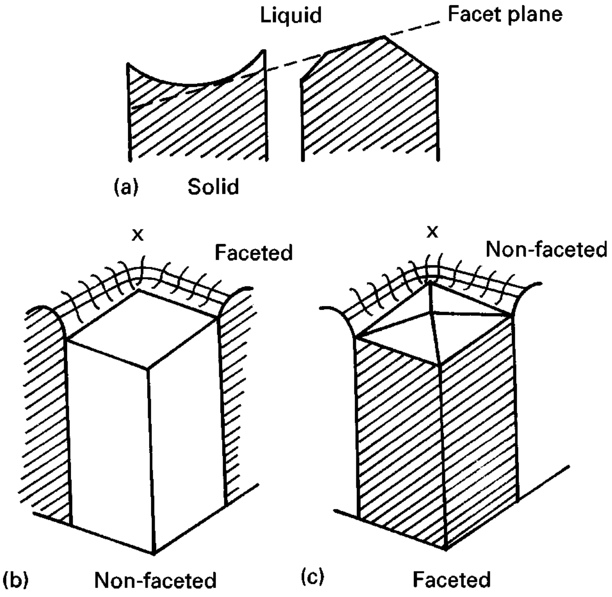

Figure 6 Curvature of the faceted phase versus its growth model: (a) convex interface, (b) non-faceted, (c) faceted.

On the contrary, if the volume fraction of a faceting phase is large enough for it to be the matrix, the curvature will be zero or concave, and microfacets will not exist. In fact, a faceted phase only occurs when the solidification conditions allow the interface curvature of the faceting phase to be convex with respect to the solid and when the interface is tangential to the faceting phase; that is, although a phase is capable of faceting, the solidification conditions may prevent it from so doing. For example, if the curvature is concave at any position, faceting does not occur because new layers of solid in adjacent regions can feed the facet plane. These features are illustrated in Fig. 6.

This is why it is easier to produce a separated eutectic from a eutectic with a lower volume fraction.

The success and validity of Croker *et al.*'s model also lies in that it can explain why the separated phases in Al–Sn, Pb–Bi systems are the components aluminium and bismuth, instead of tin and Pb_2Bi, while Hunt *et al.*'s model [7] based on the roughness parameter, cannot.

5. Conclusions

1. A separated eutectic occurs only in an anomalous eutectic under a near-equilibrium condition and the separated phase is the leading minor faceting phase.

2. The solution entropy controlling the eutectic microstructure is also valid and useful as a criterion of a separated eutectic. The anomalous eutectic in which one of its component phases possesses a solution entropy above $23\,\mathrm{J\,mol^{-1}\,K^{-1}}$ shows notable separation.

3. The hypoeutectic and ternary eutectic can also produce separated eutectic phenomena.

4. The process parameter is another important factor affecting the separated eutectic results.

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