Solidification and Structural Characteristics of $\alpha(\text{Al})\text{-Mg}_2\text{Si}$ Eutectic

Shunpu Li*, Shengxu Zhao*, Mingxiang Pan*, Deqian Zhao*,
Xichen Chen*, O. M. Barabash** and R. I. Barabash**

*Institute of Physics, Academia Sinica, Beijing 100080, P. R. China

**Institute of Metal Physics, Kiev, 252142, Ukraine

Solidification and structural characteristics of $\alpha(\text{Al})\text{-Mg}_2\text{Si}$ eutectic in the Al-Mg-Si system were investigated by thermoanalysis and directional solidification techniques. The two-phase eutectic line of $L \rightleftharpoons \alpha(\text{Al}) + \text{Mg}_2\text{Si}$, the temperature-change section of a pseudobinary $\alpha(\text{Al})\text{-Mg}_2\text{Si}$ system and the eutectic coupled zone within this section have been measured accurately. It was demonstrated that the coupled zone in the pseudobinary $\alpha(\text{Al})\text{-Mg}_2\text{Si}$ system could be described as $C = 1.35 \times 10^3 V + C_0$, where C is the molar percentage of Mg_2Si , V is the solidification velocity in m/s, C_0 is the molar percentage of Mg_2Si when the eutectic structure is obtained through a near-equilibrium solidification, and $3.65 \text{ mol}\% < C_0 < 5.0 \text{ mol}\%$. In this system, Mg_2Si is the nucleating and leading phase during eutectic growth, and the primary crystals exhibits a morphology of regular hexahedron with $\{100\}$ faces. In the eutectic alloy, the morphology of phase Mg_2Si transforms from lamellae to rods when the solidification velocity is higher than $1.1 \times 10^{-5} \text{ m/s}$. The relationship between the lamellar or interrod spacing, λ of eutectic Mg_2Si and the solidification velocity, V , fits the equation

$$\lambda^{1.93} V = 7.1 \times 10^{-17} G^{-0.414}$$

where G is the temperature gradient ahead of the solid-liquid interface in the melt, which is in K/m, λ is in m and V is in m/s.

(Received June 4, 1996)

Keywords: $\alpha(\text{Al})\text{-Mg}_2\text{Si}$ pseudobinary eutectic, directional solidification, structural characteristics

I. Introduction

Researches on eutectic solidification, especially on the two-phase eutectics, are of high theoretical and practical values. A-BC_n type monovariant pseudobinary eutectics are quite attractive, because their composition can be adjusted within a certain range. The current researches are mostly focused on Ni-, Co- and Fe-matrix high temperature alloys⁽¹⁾⁻⁽⁵⁾. There are few studies on other metal-matrix, particularly on Al-matrix monovariant pseudobinary eutectic alloys.

The pseudobinary $\alpha(\text{Al})\text{-Mg}_2\text{Si}$ eutectic alloy in the Al-Mg-Si system is a typical age-strengthening one when concentrations of Mg and Si are both low (0.4–1.5 at% Mg, 0.2–1.3 at% Si). Mg_2Si is an intermetallic compound with low density ($1.95 \times 10^3 \text{ kg} \cdot \text{m}^{-3}$)⁽⁶⁾, a relatively high melting point of 1360 K⁽⁷⁾ and an elastic modulus of 110–120 GPa and is characterized by the higher specific modulus as compared to other structural intermetallic compounds⁽⁸⁾, and these characteristics make it an ideal candidate for the strengthening phase in Al-matrix composites. It is obvious that the directionally solidified $\alpha(\text{Al})\text{-Mg}_2\text{Si}$ eutectic alloy will possess some special properties such as anisotropy strength and higher specific strength after aging treatments. Besides its monovariant feature, pseudobinary $\alpha(\text{Al})\text{-Mg}_2\text{Si}$ eutectic has advantages such as having nearly complete physical parameters available and being easy for experimental studies as Al-Al₂Cu, Al-Al₃Ni and Al-Si alloys, so it is an ideal simulative system

for eutectic solidification researches. It seems that the literature⁽⁹⁾ has paid attention to it, but this work was limited to the $L \rightleftharpoons \alpha(\text{Al}) + \text{Mg}_2\text{Si}$ monovariant eutectic line. Further research work should be focused on the $\alpha(\text{Al})\text{-Mg}_2\text{Si}$ pseudobinary temperature-change section, the pseudobinary phase diagram, and its structural characteristics, which is of high importance to the theoretical researches and production of composites.

II. Experimental Procedure

The purities of Al, Mg and Si of the raw materials used in this experiment are all above 99.99%. Alloy ingots were melted under protection of molten LiCl. Smith's thermoanalysis method⁽¹⁰⁾ was applied to measure the solidification range, $\Delta T'$ of the alloys sensitively. Directional solidification was performed by an electron-beam zone melting technique using a ring electron gun as heater. Specimen for directional solidification was placed in a graphite tube with a inner size of $\phi 8 \times 110 \text{ mm}$. The temperature gradient ahead of the solid-liquid interface in the melt was measured to be $6.3 \times 10^3 \text{ K/m}$. Investigation on the microstructures was carried out on the Neophot-21 optical microscope and the S-4200 scanning electron microscope.

III. Experimental Results and Discussions

1. Thermoanalysis

Figure 1 shows the results of thermoanalysis of transformation $L \rightleftharpoons \alpha(\text{Al}) + \text{Mg}_2\text{Si}$ in the Al-Mg-Si system, in which symbol e' represents the ternary eutectic reaction of $L \rightleftharpoons \alpha(\text{Al}) + \text{Mg}_2\text{Si} + \text{Si}$; e^0 represents the point where the temperature range of solidification equals zero in the binary eutectic reaction, $L \rightleftharpoons \alpha(\text{Al}) + \text{Mg}_2\text{Si}$; e represents any point on the binary eutectic line close to the ternary eutectic point of $L \rightleftharpoons \alpha(\text{Al}) + \text{Mg}_2\text{Si} + \text{Mg}_5\text{Al}_8$; the broken line A-A' is the position of the pseudobinary Al-Mg₂Si section. It indicates that the extremum point M of $\alpha(\text{Al}) + \text{Mg}_2\text{Si}$ eutectic line, on which the solidification range, $\Delta T'$, equals zero and its melting point T_m is the highest, does not lie on line Al-Mg₂Si that has a strict stoichiometric composition ratio (at%Mg/at%Si=2). However, the pseudobinary line shifts to the Mg-rich side and composition of the extremum point M is 10.2 at% Mg and 4.5 at% Si, which is quite different from the literature data⁽¹¹⁾. It is generally believed that the extremum point ($\Delta T' = 0$) on $L \rightleftharpoons A + \text{BC}_n$ eutectic reaction line is ought to lie on line A-BC_n in this kind of equilibrium system.

Obviously, one $L + \alpha(\text{Al}) + \text{Mg}_2\text{Si}$ three-phase region is ought to appear on the temperature-change section passing line Al-Mg₂Si now as shown in Fig. 2(a), because $\Delta T' \neq 0$. But on the temperature-change section passing line A-A', the $L + \alpha(\text{Al}) + \text{Mg}_2\text{Si}$ three-phase region degenerates into one line, which forms a standard pseudobinary $\alpha(\text{Al})$ -Mg₂Si phase diagram (Fig. 2(b)). Stability of the solid-liquid interface of directionally solidified

eutectic alloys can be characterized by:

$$\eta = \frac{G}{V} - \frac{\Delta T'}{D} \quad (1)$$

where G is the temperature gradient in the melt in front of the solid-liquid interface, V is the solidification velocity and D is the diffusion coefficient in liquid. The stability is highest when $\Delta T' = 0$, and so composition selection should lie on the pseudobinary line, A-A' when *in-situ* $\alpha(\text{Al})$ -Mg₂Si eutectic composite material is produced. This result supports the conclusions of the literature⁽⁹⁾ quite well, which was that the planar front growth in the $\alpha(\text{Al})$ -Mg₂Si monovariant eutectic reaction is more stable when the concentration ratio of magnesium to silicon in the alloy is in excess of 2. The following investigations on characteristics of $\alpha(\text{Al})$ -Mg₂Si eutectic solidification are based on Fig. 2(b).

Fig. 1 Thermoanalysis results of transformation $L \rightleftharpoons \alpha(\text{Al}) + \text{Mg}_2\text{Si}$. e' -ternary eutectic reaction of $L \rightleftharpoons \alpha(\text{Al}) + \text{Mg}_2\text{Si} + \text{Si}$; e^0 -where the temperature range of solidification equals zero in binary eutectic reaction, $L \rightleftharpoons \alpha(\text{Al}) + \text{Mg}_2\text{Si}$; e -any point on the binary eutectic line close to the ternary eutectic point, $L \rightleftharpoons \alpha(\text{Al}) + \text{Mg}_2\text{Si} + \text{Mg}_5\text{Al}_8$; A-A'-position of the section of the pseudobinary Al-Mg₂Si.

Fig. 2 Temperature-change sections: (a) passing line Al-Mg₂Si (b) passing line A-A'.

2. Eutectic coupled zone and structural characteristics of $\alpha(\text{Al})\text{-Mg}_2\text{Si}$

Three regions shown in Fig. 3 are the outcomes of standardizing the alloy structures in the concentration-solidification-velocity coordinate system according to three types: hypoeutectic, eutectic and hypereutectic, which are obtained at various solidification velocities on different composition points. Structures containing $\alpha(\text{Al})$ or Mg_2Si dendritic crystals appear within regions I and III, respectively, as shown in Fig. 4(a) and (b). Fully eutectic structure can be obtained only within region II, that is to say that the eutectic coupled zone can be approximately described as:

$$C = 1.35 \times 10^3 V + C_0 \quad (2)$$

where C is the molar percentage of Mg_2Si , V is the solidification velocity in m/s, C_0 is the molar percentage of Mg_2Si when the eutectic structure is obtained through a near-equilibrium solidification, and $3.65 \text{ mol}\% < C_0 < 5.0 \text{ mol}\%$. Eutectic structures can be obtained when the solidification conditions V and C satisfy this equation, which is of high importance to choosing techniques for production of eutectic composite materials. Certainly, this kind of linear relationship between C and V is only approximate. In fact, there should exist a more complicated form such as the exponential or logarithmic relationship.

For the eutectic structure, phase Mg_2Si has two types of morphology: one is a lamellar structure (Fig. 4(c)) when the solidification velocity is lower. Transformation from lamellar to rod-like (Fig. 4(d)) occurs when the solidification velocity is higher than $1.1 \times 10^{-5} \text{ m/s}$. The other is the structure with perfect orientation when the solidification velocity is below $1.5 \times 10^{-5} \text{ m/s}$ (when $G = 6.3 \times 10^3 \text{ K/m}$). The solid-liquid interface becomes unstable and a cellular structure appears as the solidification velocity exceeds this value (Fig. 4(e)). And the relationship between the solidification velocity, V , and

the lamellar or interrod spacing, λ , were found to fit the equation

$$\lambda^{1.93} V = 5.78 \times 10^{-16} \quad (3)$$

as shown in Fig. 5, in which λ is in m and V is in m/s.

The $\alpha(\text{Al})\text{-Mg}_2\text{Si}$ eutectic is of the nonfaceted-faceted type and phase Mg_2Si grows in a faceted way. Figure 6(a) illustrates the morphology of the primary crystals of phase Mg_2Si formed as regular hexahedrons with $\{100\}$ faces, which is a typical faceted growth. From the regularity of the morphology of Mg_2Si primary crystals, we can conclude that Mg_2Si is the nucleating phase during the solidification process of $\alpha(\text{Al})\text{-Mg}_2\text{Si}$ eutectic. It is impossible to obtain such a regular morphology if nucleation of phase Mg_2Si is subordinate to that of phase $\alpha(\text{Al})$. This point can also be seen from Fig. 6(b) on the longitudinal microstructure of the starting stage during directional solidification. Mg_2Si is not only the nucleating phase during eutectic solidification but also the leading one, its growth is in advance of that of phase $\alpha(\text{Al})$. Figure 6(c) shows the microstructure on a longitudinal section of the solid-liquid interface quenched during directional solidification of $\alpha(\text{Al})\text{-Mg}_2\text{Si}$ eutectic.

IV. Discussion

1. Estimation of the orientation of the coupled zone

There has been advanced many a theory about the coupled zone⁽¹²⁾ for its quantitative calculations. In practical applications, usually it is only necessary to estimate the orientation of the coupled zone to predict the structures (hypoeutectic, eutectic or hypereutectic) obtained under a certain solidification condition. Figure 7 shows relationship between the free-energy-composition curves for α , β and liquid phases and metastable liquidus curves (E-P and E-Q) when a eutectic alloy, A-B, solidifies under a certain undercooling ΔT . Because the formation of phases with lower free-energy enjoys priority in crystallization, phase α precipitates precedently from alloys with composition to the left of the intersecting point E' (within region I) that is formed by two common tangents of $G^\alpha\text{-}G^L$ and $G^\beta\text{-}G^L$; and to the right of this point (within region II), the crystallization of phase β enjoys priority. Symbiosis of phases α and β can only be achieved when an alloy has a composition near point E' . Undercooling of eutectic solidification is usually small, which varies from several to tens in degree. Since composition of eutectic point C_E varies little along the near-parabolic G^L curve, composition of E can be approximated as the middle point of points P and Q :

$$C_E = C_E^0 - \frac{\Delta T}{2} \left(\frac{1}{m_\alpha} + \frac{1}{m_\beta} \right) \quad (4)$$

where m_α and m_β are the slopes of the liquidus, ΔT is the undercooling and C_E^0 is the eutectic composition of equilibrium solidification ($\Delta T \sim 0$). From the Ref. (13) we have

Fig. 3 Eutectic coupled zone of $\alpha(\text{Al})\text{-Mg}_2\text{Si}$ alloy, $\circ$: hypoeutectic, $\odot$: eutectic, $\bullet$: hypereutectic.

Fig. 4 Typical directionally solidified structures of $\alpha(\text{Al})\text{-Mg}_2\text{Si}$: (a) hypoeutectic structure on longitudinal section; (b) hypereutectic structure on longitudinal section; (c) lamellar eutectic on longitudinal section; (d) rod-like eutectic on longitudinal section; (e) cellular structure on the cross section of the specimen.

$$\frac{\Delta T^2}{V} = \frac{8m_\alpha\sigma_{\alpha\beta}T_E}{\pi^2 D \Delta H \rho_s} (C_{\alpha m} - C_{\beta m}). \quad (5)$$

By substituting it into eq. (4) we have

$$C_E = C_E^0 - \left(\frac{1}{m_\alpha} + \frac{1}{m_\beta} \right) \left[\frac{2m_\alpha\sigma_{\alpha\beta}T_E}{\pi^2 D \Delta H \rho_s} (C_{\alpha m} - C_{\beta m}) V \right]^{1/2} \quad (6)$$

as for the $\alpha(\text{Al})\text{-Mg}_2\text{Si}$ alloy⁽⁹⁾: interface energy, $\sigma_{\alpha\beta} = 0.28 \text{ J/m}^2$; coefficient of diffusion of Mg_2Si in liq-

uid, $D = 5 \times 10^{-9} \text{ m}^2/\text{s}$; latent heat of α -phase, $\Delta H = 1.08 \times 10^4 \text{ J/mol}$; eutectic temperature, $T_E = 868 \text{ K}$; molar percentage of length of the eutectic line, $C_{\alpha m} - C_{\beta m} = 98 \text{ mol}$; and density of α -phase, $\rho_s = 2.7 \times 10^3 \text{ kg/m}^3$.

Slopes of liquidus of α - and β -phase, m_α and m_β were measured to be -10.2 and 16.77 per molar percentage, respectively. Substituting these parameters into eq. (6), the coupled zone could be described as:

Fig. 5 Relationship between the solidification velocity, V and the lamellar or interrod spacing, λ .

$$C_E = C_E^0 + 94.4 \sqrt{V} \quad (7)$$

where C_E and C_E^0 are in unit of mol, V is in m/s. Equations (2) and (7) have different forms because eq. (2) is obtained through simplifying the experimental results and it is approximate, while eq. (7) is through derivation. These two equation fit well at low solidification rate. But at high solidification velocity they differ much because several equilibrium parameters such as m_α and m_β , etc. are adopted in derivation of eq. (7), which do not fit the situation at high velocity.

2. Effects of temperature gradient

Theoretically, lamellar or interrod spacing, λ and solidification velocity, V satisfy the following relation⁽¹³⁾:

Fig. 6 Nucleation and front of directionally solidified $\alpha(\text{Al})\text{-Mg}_2\text{Si}$ alloys: (a) Morphology of the primary crystals of phase Mg_2Si formed as regular hexahedrons with $\{100\}$ faces; (b) Longitudinal microstructure of the starting stage during directional solidification; (c) Microstructure on a longitudinal section of the solid-liquid interface quenched during directional solidification of $\alpha(\text{Al})\text{-Mg}_2\text{Si}$ eutectic.

Fig. 7 Relationship between the free-energy curves for α , β and liquid phases and metastable liquidus curves.

$$\lambda^2 V = \frac{2\pi^2 T_E \sigma_{\alpha\beta} D_L}{\Delta H \rho_s m_\alpha (C_{\alpha m} - C_{\beta m})}. \quad (8)$$

As for the $\alpha(\text{Al})\text{-Mg}_2\text{Si}$ eutectic, the solution is

$$\lambda^2 V = 7.1 \times 10^{-17} \quad (9)$$

where λ is in m and V is in m/s, which is much different from the experimental results in this work. This is because that the influence of temperature gradient G has not been considered in theoretical studies. The influence of G cannot be ignored for nonfaceted-faceted eutectics. Considering that $G = 6.3 \times 10^3 \text{ K/m}$, equation $\lambda^{1.93} V = 5.78 \times 10^{-16}$ (λ : m; V : m/s) can be rewritten as:

$$\lambda^2 V = 7.1 \times 10^{-17} G^{-0.414}. \quad (10)$$

It is generally believed that relation

$$\lambda^2 V = K G^n \quad (11)$$

exists in eutectic systems, where n is a negative constant whose value reflects the difference between crystallization characteristics of α - and β -phase. In many alloy systems, the value of n can be empirically described as:

$$n = \frac{T_m^\alpha - T_m^\beta}{\bar{T}_m} \quad (12)$$

where T_m^α , T_m^β and $\bar{T}_m$ are the melting points of pure α - and β -phase and their average value, respectively, as tabulated in Table 1.

Table 1 Comparison of experimental values of n and calculated values of $-\Delta T_m / \bar{T}_m$.

Alloy systems	$\alpha(\text{Al})\text{-Mg}_2\text{Si}$	$\text{Al-Si}^{(14)}$	$\text{Fe-C}^{(15)(16)}$	$\text{Al-Al}_2\text{Cu}^{(17)}$
Experimental values of $-n$	0.414	0.67	0.70	$nf - nf$
$-\Delta T_m / \bar{T}_m$	0.374	0.58	0.70	0.076

3. Influence of interface energy on eutectic morphology

By calculating the geometric area, the total interface area of rod-like and lamellar eutectics with matrix phase per unit volume can be written as:

$$S_r = \left(\frac{64\pi^2}{3} \right)^{1/4} f^{1/2} \lambda_r^{-1} \quad (13)$$

$$S_L = 2\lambda_L^{-1} \quad (14)$$

where λ_r , λ_L and f are interrod spacing, lamellar spacing and volume fraction of β -phase, respectively.

From the Ref. (18), it can be seen that the ratio of interrod spacing to lamellar spacing is related to the volume fraction of the second phase, f when a certain alloy grows under a given velocity:

$$\frac{\lambda_r}{\lambda_L} = 1.743 f^{0.415} \quad (15)$$

and so

$$\frac{E_r}{E_L} = \frac{\sigma_r S_r}{\sigma_L S_L} = 1.09 \frac{\sigma_r}{\sigma_L} f^{0.085} \quad (16)$$

in which E_r and E_L are the interface energies of the two morphologies with matrix Al; σ_r and σ_L are the specific interface energies of these two morphologies with matrix Al. Since σ_r and σ_L both are the specific interface energies of phase Mg_2Si with Al, and the orientation relationship between these two phases has little influence on the specific interface energy, so σ_r / σ_L equals one approximately.

It is usually thought that the morphology with lower interface energy is selected preferentially in eutectic solidification. However it can be seen from eq. (16) that the relative magnitude of the interface energies of the two morphologies with Al has no relationship with the solidification velocity. The transformation from lamellar to rod-like morphology of phase Mg_2Si under a certain solidification velocity is not caused by the variation of the interface energies, and factors of other aspects must be considered.

V. Conclusions

(1) In Al-Mg-Si system, the point where the solidification range of $\alpha(\text{Al})\text{-Mg}_2\text{Si}$ eutectic, $\Delta T'$ equals zero, does not lie on the pseudobinary line of Al-Mg₂Si with strict stoichiometric composition ratio (at%Mg/at%Si=2), but it shifts to the Mg-rich side. The highest

stability of the solid-liquid interface is achievable when directional solidification is carried out on this composition.

(2) Eutectic structure is gained exclusively when the temperature gradient equals $6.3 \times 10^3 \text{ K/m}$ and the solidification condition of $\alpha(\text{Al})\text{-Mg}_2\text{Si}$ satisfies

$$C = 1.35 \times 10^3 V + C_0$$

where V is in m/s , and $3.65 \text{ mol}\% < C_0 < 5.0 \text{ mol}\%$. Otherwise, hypoeutectic or hypereutectic structures containing dendrites of $\alpha(\text{Al})$ or Mg_2Si appear.

(3) Mg_2Si acts as the nucleating and leading phase during solidification of $\alpha(\text{Al})\text{-Mg}_2\text{Si}$ eutectic. Morphology of phase Mg_2Si transforms from lamellar to rod-like when the solidification velocity is higher than $1.1 \times 10^{-5} \text{ m/s}$; and cellular structures appear instead of planar structures when the solidification velocity is higher than $1.5 \times 10^{-5} \text{ m/s}$. Changes of the eutectic morphology have no relation with the variation of interface energy. The relationship between the lamellar or interrod spacing, λ of phase Mg_2Si and solidification velocity, V , satisfies the equation

$$\lambda^2 V = 7.1 \times 10^{-17} G^{-0.414}$$

where λ is in m and V is in m/s .

In some eutectic systems, this relation can be written as:

$$\lambda^2 V = KG^n$$

in which

$$n = \frac{T_m^\alpha - T_m^\beta}{\bar{T}_m}$$

where T_m^α , T_m^β and $\bar{T}_m$ are the melting points of pure α - and β -phase and their average value, respectively.

REFERENCES

- (1) J.-Z. Li, M. Kaya and R. W. Smith: *J. Mater. Sci.*, **29** (1994), 1083.
- (2) J.-Z. Li, M. Kaya and R. W. Smith: *J. Crys. Growth*, **133** (1993), 175.
- (3) O. M. Barabash, P. B. Gorskaya, T. N. Leokaya and S. P. Oskaderov: *Powder Metall. (in Rus.)*, **5** (1990), 67.
- (4) B. H. Glinev, O. M. Barabash and T. N. Leokaya: *Metal Physics*, **5** (1982), 20.
- (5) F. D. Lemkey and E. R. Thompson: *Metall. Trans.*, **2** (1971), 1537.
- (6) M. Riffel and J. Schilz: *Scripta Metall. Mater.*, **32** (1995), 1951.
- (7) A. A. Nayeab-Hashemi and J. B. Clark: *Bull. Alloy Phase Diagr.*, **5** (1984), 584.
- (8) G. H. Li and Q. P. Kong: *Scripta Metall. Mater.*, **32** (1995), 1435.
- (9) J. Kaneko: *J. Japan Inst. Metals*, **37** (1973), 780.
- (10) C. S. Smith: *Trans. Am. Inst. Min. Met. Eng.*, **137** (1940), 236.
- (11) L. F. Mondolfo: *Aluminum Alloys, Structure and Properties*, Butterworth London, (1976), p. 566.
- (12) K. A. Yakason: *Trans. Met. Soc. AIME*, **242** (1968), 1275.
- (13) M. C. Flemings: *Solidification Processing*, Metallurgical Industry, (1981), p. 105.
- (14) B. Toloui and A. Hellawell: *Acta Metall.*, **24** (1976), 565.
- (15) E. Schurman and H. Loblich: *Giessereiforschung*, **29** (1977), 67.
- (16) E. Schurman and H. Loblich: *Paper in 43rd IFC*, Bucharest, (1967), p. 17.
- (17) R. Elliott: *Eutectic Solidification Processing*, Butterworth, (1983), p. 104.
- (18) P. Magnin and R. Trivedi: *Acta Metall. Mater.*, **39** (1991), 453.