Unidirectional Solidification Structure of 
Al–In Monotectic Alloys*

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Monotectic Al-17.5 mass % In alloys were solidified unidirectionally at various growth rates from $2.8 \times 10^{-7}$ to $1.11 \times 10^{-2}$ m/s and temperature gradients from 500 to 8500 K/m. When a temperature gradient is constant, the microstructure changes in the sequence with increasing growth rates: fibrous composite structure → periodical and regular array of L2 (In) droplets → random dispersion of L2 droplets in the aluminum matrix. The critical growth rate to form regular composite structures increases, as the temperature gradient increases. The monotectic composite structure, i.e., the regular arrangement of L2 fibers or L2 droplets in the aluminum matrix is obtained at $G/R$ more than $10^6$ K·s/m². The inter-fiber spacing $\lambda$ of L2 is related to growth rates $R; \lambda = KR^{-1/2}$, $K$ being $2.8 \times 10^{-8}$ m$^{1.5}$ s$^{-0.5}$.

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I. Introduction

Al–In alloy is one of the typical monotectic aluminum alloys as shown in Fig. 1(1). The homogeneous liquid $L_1$ containing 17.5 mass % In transforms at 912 K to the Al solid solution S and the indium rich liquid $L_2$ simultaneously through the monotectic reaction. This alloy has such proprietary characteristics that both aluminum and indium are almost insoluble to each other in the solid state, $L_1$ and $L_2$ are greatly different in density from each other, and the alloy has a liquid miscibility gap widely extending in the diagram. A few works have been made concerning the monotectic solidification, and the present authors have reported on the monotectic solidification of free-directionally solidified Cu–Pb(2) and Al–In alloys(3).

A monotectic reaction is similar to the eutectic reaction except that one of the products is liquid. When Bi–Se(4), Cu–Pb(2)(5), Al–Bi(6)(7) and Al–In(3)(8) alloys solidify unidirec-

tionally, fibrous or rod-like composite structures crystallize. Recently Grugel et al. reported the unidirectional solidification of Al–In alloys at the high temperature gradient of 19000 K/m, suggesting that fibrous and arrayed droplet composite structures formed at growth rates below $5.0 \times 10^{-6}$ m/s and $(5-10) \times 10^{-6}$ m/s, respectively(8).

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A metallographical work is made in the present work on Al–In monotectic alloys solidified unidirectionally at various growth rates under different temperature gradients.

II. Experimental Procedures

1. Alloy preparation

Monotectic Al–17.5 mass% In alloys were prepared from 99.99 mass% purity Al and 99.99 mass% purity In. The alloys were melted under argon atmosphere in high purity alumina crucibles. The molten alloys were prepared in the following way to overcome difficulties in melting practice caused by miscibility gap and differences in densities and melting points between L₁ and L₂. Small pieces of In were added intermittently to the molten Al at a temperature 150 K above the monotectic point, being stirred by argon gas bubbling for 1.8 ks (0.5 h). The melt was degassed by the use of 1.0 mass% CCl₃·CCl₃.

2. Unidirectional solidification

The alloys of monotectic composition were unidirectionally solidified in argon atmosphere using two different experimental apparatuses shown by (a) and (b) in Fig. 2; (a), the molten alloys were poured into a graphite mold 30 mm in O.D., 10 mm in I.D. and 100 mm in length, and they were solidified unidirectionally upward from the bottom by water cooling the bottom and pulling the holding furnace upward. (b), unidirectional solidification was achieved by driving the alumina crucible downward out of the induction coil at a given rate. A graphite tube was used as a susceptor. A high purity alumina crucible 17 mm in O.D. and 13 mm in I.D. was first filled with sample ingots 12 mm in dia. and 80 mm in length, which were cast in a graphite mold and solidified at a rate of 150 K/s, up to approximately 300 mm in length and then was driven into the induction coil for over 5 h for remelting, subsequently being withdrawn downward at a given growth rate. Solidification conditions such as growth rate and temperature gradient were measured by the use of 3–4 C.A. thermocouples inserted in the mold cavity. In order to change the growth condition, the driving rate of the crucible and/or the holding furnace, mold material and chill block material were changed from experiment to experiment. The range of growth rates and temperature gradients were \(2.8 \times 10^{-7} - 1.1 \times 10^{-2} \text{ m/s} (1-4 \times 10^{-4} \text{ mm/h})\) and 500–8500 K/m respectively.

III. Results and Discussion

1. Microstructures at high growth rates

Solidified L₂ droplets are dispersed at random in the Al matrix solidified at high growth rates as shown in Fig. 3. Small L₂ droplets seem to be aligned discontinuously along the growth direction, while coarser ones are aligned along cell boundaries. These structures coarsen, as the growth rate lowers. Random dispersion of L₂ droplets is achieved at high growth rate as in Al–3.4 mass% Bi monotectic alloys solidified unidirectionally at a high growth rate \((3.3 \times 10^{-4} \text{ m/s})\).

2. Microstructures at low growth rates

Figure 4 shows microstructures solidified at low growth rates under low temperature gradients 600 to 1000 K/m. L₂ droplets become to align along the growth axis at a rate \(3.1 \times 10^{-6} \text{ m/s}\) and L₂ phases along monotectic cell boundaries are elongated along the growth direction. Spherical L₂ droplets are arrayed most orderly at the rate \(1.1 \times 10^{-6} \text{ m/s}\). They seem to align exactly parallel both to the
growth axis and growth front at almost regular intervals. Band structures of L₂ droplets are formed on the micrographic section having a slight angle to the growth direction. There occurs a composite structure of regularly spaced L₂ fibers which are nearly equal in diameter, linear and of smooth surface without branches and arrayed at an average spacing $28 \times 10^{-6}$ m. A monotectic composite structure, regular arrangement of L₂ fibers of L₂ droplets in the Al matrix, is achieved only at growth rates $1 \times 10^{-6}$ m/s or less under temperature gradients 600 to 1000 K/m.

3. Influence of temperature gradient on growth rate to form monotectic composite structures

Fibrous composite structures are obtained even at $3.6 \times 10^{-6}$ m/s under large temperature gradients 5000 to 6000 K/m. Figure 5 shows microstructures solidified at $0.28 \times 10^{-6}$, $1.1 \times 10^{-6}$ and $2.5 \times 10^{-6}$ m/s, respectively. Average fiber spacings are plotted against the growth rate in Fig. 6. The log $\lambda$–log $R$ straight line, having gradient $-0.45$ close to $-0.5$ indicates that the growth of fibrous monotectic composite approximately obeys a diffusion controlled form $\lambda = KR^{-1/2}$, (where $\lambda$; inter-fiber spacing, $R$; growth rate and $K$;...
constant). It is a common relationship among lamella or rod eutectic composite structures, a constant $K \approx 2.6 \times 10^{-8} \text{ m}^{1.5} \text{s}^{-0.5}$ being a little larger than $K$ of rod-like eutectic alloys. $\lambda$ under the temperature gradient 2500 K/m and under 19000 K/m according to Grugel et al. are also plotted in this figure. These plots show that the inter-fiber spacing depends on the temperature gradient and that the latter affects the formation of $L_2$ fibers. The critical growth rate to form fibrous composite structures shifts toward higher growth rate with increasing temperature gradient.

4. Transition from $L_2$ fibers to $L_2$ droplets

Grugel et al.\cite{Grugel} described that Al–In monotectic alloys solidify to form fibrous composite structures under 19000 K/m at growth rates below $5.0 \times 10^{-6}$ m/s, regularly aligned $L_2$ droplet composite structures at $(5 \text{ to } 10) \times 10^{-6}$ m/s and random dispersion of $L_2$ droplets at growth rates $10 \times 10^{-6}$ m/s or more. However, in the present work, the $L_2$ fibrous composite and the regularly arrayed $L_2$ droplet
composite coexist. A temporary structural transition from $L_2$ fiber to $L_2$ droplet is also observed in the alloys solidified at the rate of $0.44 \times 10^{-6}$ m/s under 600 K/m, as shown in Fig. 7. The fibrous structure turns to the arrayed structure of droplets temporarily and to the fibrous structure again. The arrayed structure of $L_2$ droplets may be formed by necking down, pinching off and spheroidizing of $L_2$ fibers during cooling below the monotectic temperature. Grugel et al. stated that such a regular structure never occurs by shape perturbation during cooling below the monotectic temperature\(^{(8)}\). Fairly periodical necking of $L_2$ fibers is often observed, however, when fibrous and droplet structures coexist as shown in Fig. 8. Necking down, pinching off and spheroidizing of $L_2$ fibers may result in the arrayed structure of spherical $L_2$ droplets.

5. Disintegration of regular composite structures

The arrayed structure of $L_2$ droplets is obtained even at the growth rate of $2.5 \times 10^{-6}$ m/s at a lower temperature gradient, but the arrangement of $L_2$ droplets becomes to be disordered at some monotectic cell grains, as shown in Fig. 9. Solidified structures are no longer of regular composite at the higher growth rate $4.4 \times 10^{-6}$ m/s, but random dispersion of fine $L_2$ droplets is seen, as shown in Fig. 10.

Structures observed in the present work are classified according to the temperature gradient ($G$) and the growth rate ($R$) in Fig. 11. Namely, the regular fibrous composite or the regularly arrayed droplet composite is obtained at $G/R > 10^9$ K·s/m² or more. Regularly arrayed and longer $L_2$ fibers are observed, on the other hand, at $G/R$ much higher than $10^9$ K·s/m². Regularly and periodically arrayed structures of $L_2$ droplets begin to take fibrous composite structures, as $G/R$ approaches $10^9$ K·s/m². An intermittent transition from fiber to droplet or droplet to fiber is found at the critical condition of $G/R > 10^9$ K·s/m². $L_2$ droplets randomly disperse, when $G/R$ lowers to $10^9$ K·s/m² or less. $G/R$ is one of the parameters which define solid-liquid interface stability in the unidirectional solidification. Figure 11 shows that the
formation and its transition of monotectic composite structures depend on the solid-liquid interface morphology and its transition manner.

IV. Summary

Al-17.5 mass%In alloys of monotectic composition were solidified unidirectionally at various growth rates and temperature gradients. When the temperature gradient is constant, the structures change in the sequence, fibrous composite structures→periodically and regularly arrayed structures of L₂ droplets→random dispersion of L₂ droplets in the aluminum matrix with increasing growth rate. The critical growth rate to form regular composite structures increases, as the temperature gradient steepens. The monotectic composite structure, i.e., the regular arrangement of L₂ fibers or L₂ droplets in the aluminum matrix is formed at $G/R = 10^9$ K·s/m² or more. The inter-fiber spacing ($\lambda$) of L₂ is related to the growth rate ($R$) by $\lambda = KR^{-1/2}$ similarly to lamella or rod eutectic composite structures, $K$ being $2.8 \times 10^{-8}$ m²·s⁻¹. The formation of fibrous monotectic composite depends on the diffusion controlling process. Regularly arrayed L₂ droplets seem to be formed by periodical forming of L₂ droplets at the monotectic growth front, because the array of L₂ droplets corresponds to the solid-liquid interface morphology. Necking down, pinching off and spheroidizing of L₂ fibers during cooling after the monotectic growth may result in the regularly arrayed structure of L₂ droplets.

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REFERENCES