Unidirectional Solidification of Aluminum-Indium Monotectic Alloys by Ohno Continuous Casting*

Shumpei Ozawa[1], Tetsuichi Motegi[2] and K. Kuribayashi[1]

[1]*Institute of Space and Astronautical Science, Japan Aerospace Exploration Agency, Sagamihara 229-8510, Japan*
[2]*Department of Mechanical Engineering and Science, Chiba Institute of Technology, Narashino 275-0016, Japan*

The vertical Ohno Continuous Casting (OCC) process was used to examine the possibility of casting Al-In monotectic alloys with a homogeneous microstructure. Three compositions, Al-17.3 mass%In, Al-20 mass%In, and Al-25 mass%In were used in this study. Al-In alloy ingots with a diameter of 8 mm and a length of 400 mm could be continuously cast by controlling the temperature and solidification velocity of the melt regardless of the alloy compositions. The Al-In alloy ingots had a very beautiful surface and a unidirectional macrostructure. Furthermore, the Al-In alloys exhibited a good distribution of β-In particles throughout all sections without any segregation of β-In phase.

1. Introduction

Monotectic system alloys, such as Al-In alloys and Cu-Pb alloys, are characterized by a miscibility gap in liquid state.[1] When a melt with a hyper-monotectic composition falls into the immiscible liquid region from a single-liquid phase temperature, it decomposes into two liquid phases with different compositions. The different densities between the spatial phases always result in gravity-induced sedimentation of the melts, which is accounted for by the Navier-Stokes equations.[1–3] Therefore, it is difficult to produce hyper-monotectic system alloys with homogeneous microstructures. Many studies have been conducted on producing the monotectic system alloys with homogeneous microstructures using various techniques, such as unidirectional solidification, rapid solidification, and solidification in microgravity.[3–10] Although these techniques effectively produce a homogeneous microstructure of the alloys with monotectic composition, little success has been reported for the alloys with hyper-monotectic compositions.

It has been reported that a heated-mold continuous casting technique, called the Ohno Continuous Casting (OCC) process, can produce homogeneous microstructures in various metals and alloys.[11–17] A heated mold prevents nucleation on the mold wall; the heat of the melt is extracted only through the cast products in this technique. Therefore the cast products always have a single crystal or unidirectional microstructure along the cast direction. Furthermore, the ingots have a very beautiful surface in which the melt is solidified outside of the mold without the friction from the mold. However, the effects of the OCC process on the microstructures of the monotectic system alloys have never been studied. If the OCC process can be applied to solidifying monotectic alloys, homogeneous microstructures of the alloys may be produced.

In this study, the OCC process produced Al-In monotectic alloys. The morphology and distribution tendency of the minority phase of β-In were examined to investigate the
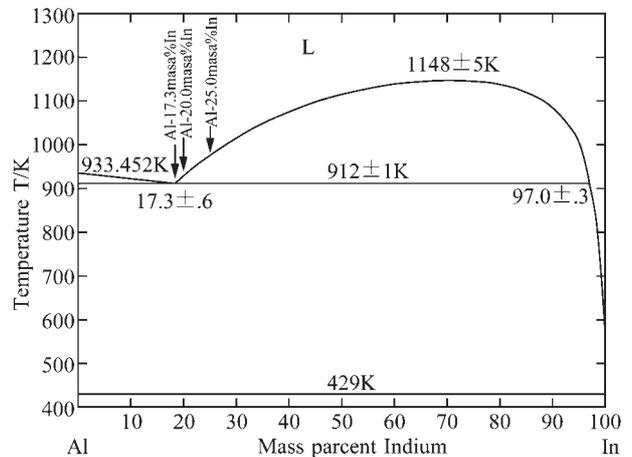
Fig. 1   Al-In binary phase diagram.

influence of the OCC process on the microstructure of Al-In monotectic system alloys. One specific objective of the investigation was to produce the homogeneous microstructure of Al-In alloys with hyper-monotectic compositions by the OCC process.

2. Experimental Procedure

Figure 1 shows an Al-In binary phase diagram, where the sample compositions used in this study are arrowed; monotectic composition alloy (Al-17.3 mass%In) and hyper-monotectic composition alloys (Al-20, 25 mass%In) were used. Figure 2 presents a schematic diagram of the experiment set-up, which consists of an electric furnace, a graphite mold, a dummy bar of stainless steel, and a displacer block of Al_2O_3 for controlling the melt level. Segments of 99.99 mass% Al and 99.99 mass% In were charged into an Al_2O_3 crucible placed in the electric furnace. The raw materials were melted and were kept above the single-liquid-phase temperature for the alloy compositions in an argon atmosphere. The melt and graphite mold temperatures were monitored by thermocouples. The dummy bar was slightly immersed into the melt and then raised gradually. The melt was dragged by the surface tension between the dummy bar
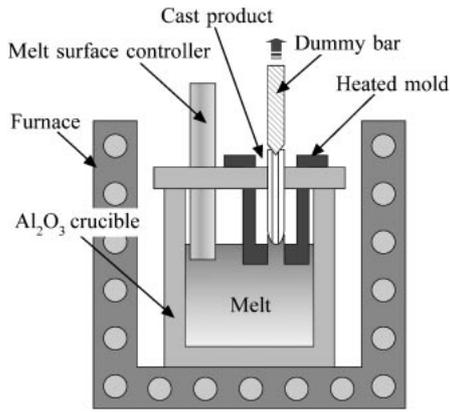
Fig. 2   Schematic diagram of the vertical OCC process.

and the melt, and solidified continuously outside the heated mold. Simultaneously, the melt was continuously fed into the mold by lowering the displacement block for controlling the melt level. The resultant cast product was a rod with 8 mm diameter and 400 mm long.

The samples were cut along their solidification direction. The macrostructures were observed after polishing and etching in copper (II) chloride 30 mass% solution. The microstructures were observed by optical microscopy after polishing. Distribution tendency of β-In particle was examined by counting the number of it in ten sets of 1 mm $\times$ 1 mm regions of the microstructures according to the particle size.

3.   Results

Figure 3 shows the Al-In alloy ingots produced by the OCC process. Regardless of the alloy compositions, the surfaces of the ingots are classified into three types, beautiful surface, constricted surface, and cracked surface. The ingots with the beautiful surface are obtained by choosing the proper
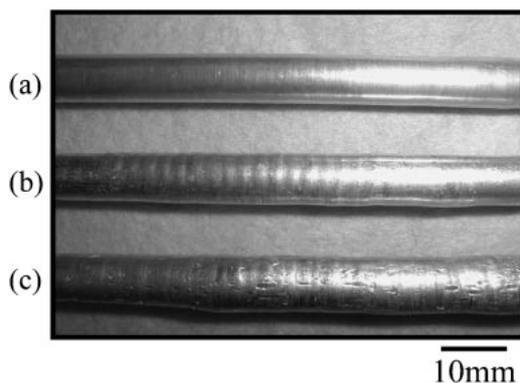
Fig. 3   Al-In alloy ingots produced by the OCC process. (a) beautiful surface, (b) constricted surface, and (c) cracked surface.

casting velocity and mold temperature; the solidification front is located outside the mold and the casting velocity is equal to the solidification velocity. The ingots with constricted surfaces are observed when the casting velocity or mold temperature is inappropriate and the casting velocity does not balance the solidification velocity, even though the solidification front is located outside the mold. The ingots with the cracked surface are observed when the casting velocity or mold temperature is lower than appropriate and the solidification front shifts into the mold.

A major problem in producing monotectic system alloys is segregation of the minority phase. Significantly different densities between the spatial phases always cause gravity-induced sedimentation of the melts. Therefore, it is difficult to produce monotectic system alloys with target compositions and homogeneous microstructures by unidirectional solidification. In order to examine the content of β-In in the Al-In alloys produced by the OCC process, the sample compositions were calculated by the following simultaneous equations,

$$w = w_{Al} + w_{In} \tag{1}$$

$$V = \frac{w_{Al}}{\rho_{Al}} + \frac{w_{In}}{\rho_{In}} \tag{2}$$

$$P = \frac{w_{In}}{w} \times 100 \tag{3}$$

Where w is the sample mass, w_{Al} and w_{In} are the mass of aluminum and indium in the sample, V is the sample volume, ρ_{Al} and ρ_{In} are the densities of aluminum and indium, and P is the composition of In. Table 1 lists the estimated compositions of the Al-In alloys with 20 mm in length cut from various sections. Regardless of the sample compositions or sections, the estimated composition is similar to the target composition. This suggests that the Al-In alloy ingots produced by the OCC process do not have significant sedimentation of the β-In phase.

Figure 4 depicts the longitudinal section macrostructures of the Al-In alloys with a beautiful surface. The macrostructures are observed at two positions, 50 mm and 300 mm from the dummy bar. Regardless of the alloy compositions, unidirectional macrostructures are observed in the sections 300 mm from the dummy bar though no appreciable unidirectional macrostructures are observed in the sections 50 mm from the dummy bar. This implies that the heated mold prevents new nucleation on the mold wall and inside the melt. The number of crystal is reduced by competitive growth. When the monotectic system alloys are produced by unidirectional solidification methods like the zone-melting or the Bridgman method, macro-segregations such as a banded-structure or large gravity-induced segregations are often observed in the macrostructures.[2,5] However, no macro-segregations are observed in the macrostructures of the Al-In

Table 1   Estimated composition of Al-In alloys produced by the OCC process in sections 100, 200 and 300 mm from the dummy bar.

Target composition	Estimated indium content at various sections (mass%)		
	100 mm	200 mm	300 mm
Al-17.3 mass%In	17.01	16.47	16.60
Al-20.0 mass%In	19.99	20.09	19.79
Al-25.0 mass%In	24.60	25.02	24.68
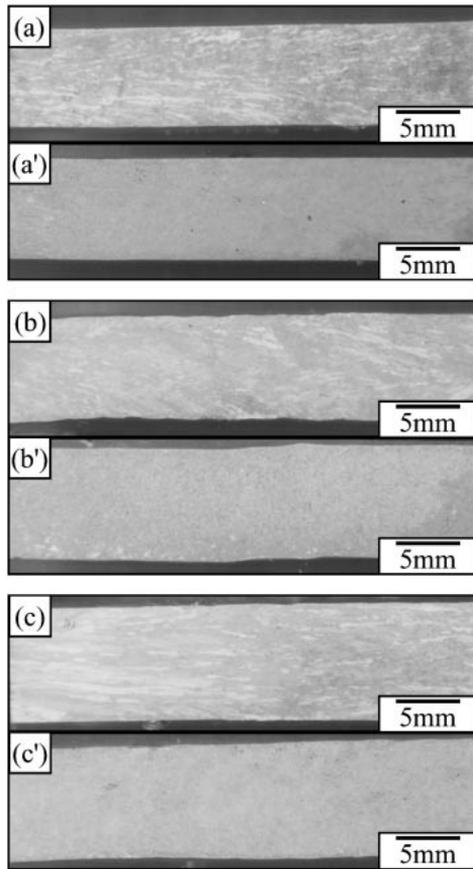
Fig. 4   Macrostructures of (a) Al-17.3 mass%In, (b) Al-20.0 mass%In, and (c) Al-25.0 mass%In alloys produced by the OCC process at 50 mm from dummy bar. (a′), (b′) and (c′) depict the those at 300 mm from dummy bar.

no appreciable unidirectional microstructures are observed, though the unidirectional macrostructures can be seen; the particle distribution differs in region between equiaxed grains and unidirectional columnar grains. Due to the limited observation region, the unidirectional solidification seems not to be achieved in microstructures of the Al-17.3 mass%In and Al-20 mass%In alloys. However, the crystallization of α-Al and distribution of β-In, probably, have some directionality along the casting direction when those are observed within millimeter range. The reason why the microstructures differ in sample compositions between equiaxed grains and unidirectional columnar grains is explained in next section.

We examined the size distribution of β-In particles to clarify the distribution of that in the Al-In alloys produced by the OCC process. The result is shown in Fig. 6. The fraction of β-In particles with diameters of 0 to 5 μm is the largest in the Al-17.3 mass% In alloy produced by the OCC process. The fraction of β-In particles with diameters of 0 to 5 μm is reduced, and comparatively large particles with diameters of 15 to 20 μm are generated in the Al-20 mass%In alloy. Increasing the In content decreases the number of β-In particles of 0 to 5 μm and increases the number of large particles. When In content is increased in an Al-In alloy, the volume fraction of β-In phase increases in the immiscible liquid region. Furthermore, the melt takes longer to solidify because the single-liquid-phase temperature rises as the In content increases from 17.3 mass% to 25 mass%. Thus, the spatial β-In phase may collide and coalesce in the immiscible liquid phase region.

alloys produced by the OCC process, even in the hyper-monotectic composition alloys. This confirms that the OCC process prevents the significant segregation of the β-In phase.

Figure 5 illustrates the microstructures of the Al-In alloys with a beautiful surface. The microstructures were observed 300 mm from the dummy bar and correspond to Figs. 4(a), (b) and (c). The white and black regions are α-Al and β-In phases, respectively. Regardless of the sample compositions, the microstructures of the Al-In alloys exhibit a good distribution of the β-In particles throughout all sections. Large particles and coagulation of β-In phase can not be observed in the microstructures even in the Al-In alloys with hyper-monotectic compositions. Furthermore, the sample compositions are practically the same as the target compositions estimated from simultaneous equations (cf. Table 1). These results indicate that the OCC process can produce very homogeneous Al-In alloys with target compositions.

Excluding the microstructure of the Al-25 mass%In alloy,

Fig. 6   Size distribution of β-In particles of Al-In alloys produced by the OCC process.

Fig. 5   Microstructures of (a) Al-17.3 mass%In, (b) Al-20.0 mass%In, and (c) Al-25.0 mass%In alloys produced by the OCC process.

4. Discussion

The OCC process can produce very homogeneous Al-In alloys with target compositions even in hyper-monotectic composition alloys. However, the distribution tendency of β-In particle differs in regions between equiaxed grains (Al-17.3 mass%In and Al-20 mass%In alloys) and unidirectional columnar (Al-25 mass%In alloys) as shown in Fig. 5. The microstructures of the Al-In alloys with monotectic composition produced by unidirectional solidification using the Bridgman method strongly depend on the growth velocity R and temperature gradient G.[4,5] When G/R value is lower than 10^{-9} Ksm^{-2}, the Al-In alloys exhibited a random dispersion of β-In particles. Al-In alloys solidified at G/R value around 10^{-9} Ksm^{-2} exhibited microstructures with a good alignment of β-In particles. The microstructures of the Al-In alloys solidified at G/R value exceeding 10^{-9} Ksm^{-2} consisted of a fibrous composite of β-In phase. We therefore investigated the growth velocity and temperature gradient of the alloys produced by the OCC process. The alloys produced by the OCC process had G/R values of 4.6×10^8 Ksm^{-2} (Al-17.3 mass% In), 4.4×10^8 Ksm^{-2} (Al-20 mass% In), and 3.3×10^9 Ksm^{-2} (Al-25 mass% In). The relationship between the morphology and G/R value of the Al-In alloys produced by the OCC process is similar to that of the alloys produced by the Bridgman method which is only for alloys with monotectic composition.[5,6] The relationship between G/R value and the microstructure in the Al-In alloys produced by the Bridgman method may be applied for the Al-In alloys produced by the OCC process. It must be noted that the relationship also applies to alloys with hyper-monotectic compositions produced by the OCC process.

Some doubt remains about the relationship between the microstructure and G/R values since only the OCC process produces the homogeneous microstructures of hyper-mono-tectic composition alloys, though almost the same G/R values are achieved in the OCC process and the Bridgman method. The growth velocity in the OCC process is higher than that in the Bridgman method; the growth velocity of the alloys are 6.7×10^{-5} ms^{-1} (Al-17.3 mass%In), 8.0×10^{-5} ms^{-1} (Al-20 mass% In), and 8.5×10^{-5} ms^{-1} (Al-25 mass% In). These values are over 10 times greater than the alloys produced by the Bridgman method.[5] Such a high growth velocity may prevent the sedimentation of the β-In phase in the alloys during solidification. In brief, we have to pay attention to not only the G/R value but also growth velocity during solidification of the monotectic system alloys.

The relationships among the G/R value, growth velocity, and microstructures should be theoretically clarified. It is well known that the theoretical explanations for composite growth are usually based on the classical Jackson Hunt model for eutectics.[18] Several researchers have extended this model for monotectic alloys.[19,20] However, the calculation results greatly differ from the experimental data.[20]

The above results suggest that the OCC process is more suitable for producing homogeneous Al-In alloys than other unidirectional solidification methods because this method can produce very homogeneous alloys even in the hyper-monotectic alloys. The microstructures of the Al-In alloys produced by the OCC process seem to depend on the G/R values and growth velocity. It is difficult to control the G/R value and growth velocity in the vertical OCC process used in this study because of the cooling of melt. However, the horizontal OCC process can easily control the cooling rate of the melt. Further research into the horizontal OCC process would clarify the influence of G/R value and growth velocity on the microstructures of Al-In alloys.

5. Conclusion

The Ohno Continuous Casting process produced Al-In monotectic system alloys with a monotectic composition of Al-17.3 mass%In, and hyper-monotectic compositions of Al-20.0 mass%In and Al-25.0 mass%In. Al-In alloys with three types of surfaces (beautiful surface, cracked surface, and constricted surface) were obtained depending on the casting velocity and heated mold temperature. The estimated compositions of the resultant alloys were almost the same as target compositions. The resultant alloys had unidirectional macrostructures regardless of alloy compositions. No appreciable unidirectional microstructure was observed, excluding the Al-25 mass%In alloy. The Al-In alloys consisted of a very homogeneous microstructure throughout all sections. The particles in the β-In phase became slightly larger as the alloy composition was increased in the Al-In alloys.

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