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Directional solidification of rod eutectics in $NaNO_3$-NaCl system

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Abstract The partial phase diagram of $NaNO_3$-NaCl system was investigated and the eutectic temperature was determined as 294.5 °C. A typical rod eutectics of $NaNO_3$-4.56 wt%NaCl was directionally solidified. The results of interrod spacing, λ_E, as a function of growth velocity, V, were obtained as $\lambda_E V^{0.39} = 5.26$ (temperature gradient, $G_l = 21.4$ °C/mm) and $\lambda_E V^{0.32} = 5.45$ ($G_l = 3.9$ °C/mm) and the exponent numbers of growth velocity were smaller than the theoretical value, 1/2. The sample rotation applied during directional solidification made the interrod spacing decrease slightly.

Key words Rod eutectics, $NaNO_3$-NaCl system, Directional solidification

1. Introduction

It is well known to produce in-situ composites with applying the directional solidification to eutectic alloys where two distinctively different solid phases simultaneously solidify from the liquid. Such a uniformly aligned composite to give superior material properties can be used in the various fields. Since the work of Guthrie [1], the numerous investigations of eutectic alloys have been done and some fundamental information about eutectic microstructure has been found. The important relationships between the phase spacing (λ_E) and solidification processing parameters characterize the resulting eutectic microstructure and consequently mechanical and physical properties. Especially Jackson and Hunt [2] provided a comprehensive theory to explain the experimental results of eutectic systems. In addition, some convection during the solidification leads to the variation of eutectic spacing and it was reported that the microgravity condition to reduce the gravity-induced convection resulted in refining microstructure for rod eutectics, Bi-MnBi [3]. The changes of microstructure can be explained by different convection conditions between micro g and 1 g. Therefore in this study $NaNO_3$-NaCl system to show the fibrous eutectics in a hexagonal array has been selected and directionally solidified with varying processing parameters to investigate the variation of eutectic spacing. Also the sample rotation during directional solidification has been applied to change some convection effects on earth instead of microgravity condition.

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2. Experimental Procedure

To determine the partial phase diagram of $NaNO_3$-NaCl system, a series of compositions from pure $NaNO_3$ to $NaNO_3$-9.9 wt%NaCl were melted and cooled in the pot furnace. The liquidus and eutectic temperatures were measured from the data obtained with computer data acquisition system. To investigate the fibrous nature of eutectic $NaNO_3$-4.56 wt%NaCl with directional solidification, appropriate weights of pure materials were melted together and the homogeneous liquid was sucked up into 5 mm ID quartz tube connected to vacuum line. The sample tubes were then mechanically driven into a Bridgman type furnace, held for 0.5 hour and subsequently withdrawn vertically downward through a water-cooled torroid at imposed growth rates. The temperature gradients at the solid-liquid interface were measured with thin thermocouples inserted into melt and two different temperature gradients, 21.4 and 3.9 °C/mm, were used. In order to give sample tube some rotation during directional solidification a small motor was coupled to the end of tube and the different rotation rates were used with varying the applied motor voltage. The processed samples were broken perpendicular and parallel to the growth direction, coated with gold and examined with scanning electron microscope.

3. Results and Discussion

The partial phase diagram of $NaNO_3$-NaCl system is

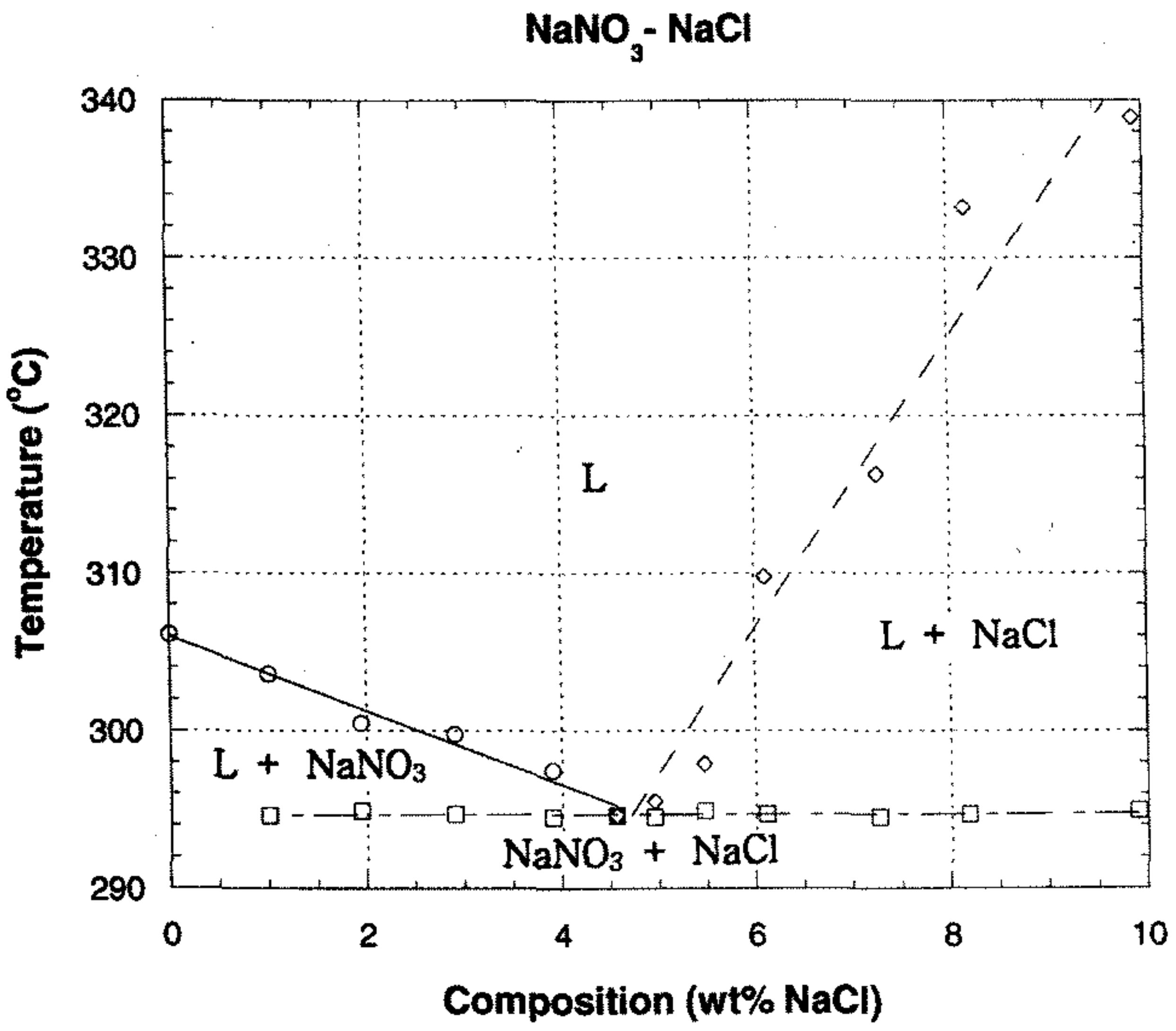

Fig. 1. The partial $NaNO_3$-NaCl phase diagram determined in this study.

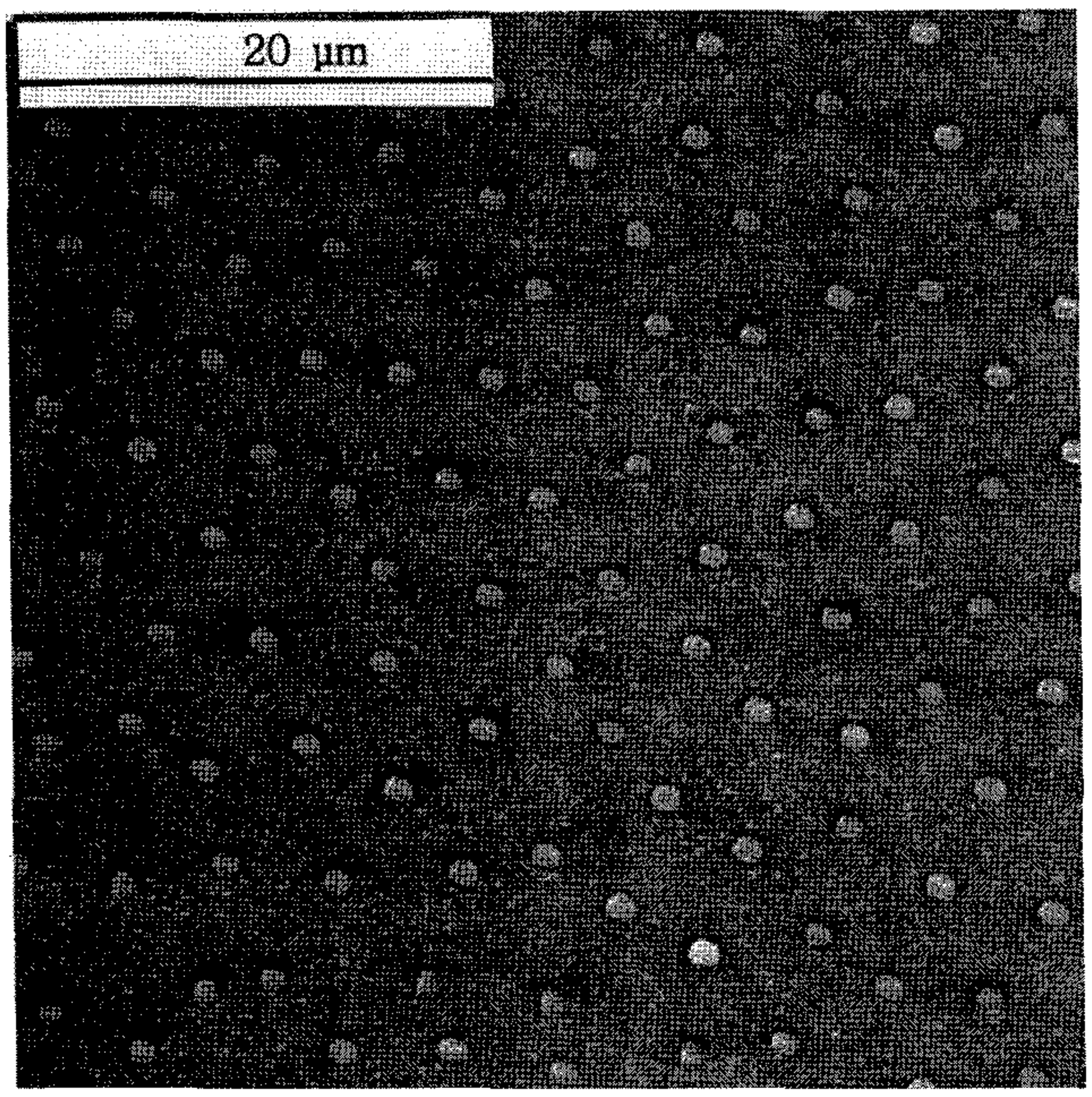

Fig. 2. The photograph of transverse microstructure of rod eutectic, $NaNO_3$-4.56 wt%NaCl directionally solidified.

shown in Fig. 1 and is very similar to the previous results [4] and those of other eutectic metallic systems. The eutectic temperature was determined as 294.5 °C. Fig. 2 is a typical transverse microstructure of rod eutectic, $NaNO_3$-4.56 wt%NaCl, which consists of uniformly spaced NaCl rods in a hexagonal array within $NaNO_3$ matrix. Therefore the relation presented by Jacobi and Schwerdtfeger [5] was used to compute the interrod spacing, λ_E,

$$\lambda_E = \{4A/(3^{1/2}(2N - (12N - 3)^{1/2} + 1))\}^{1/2} \quad (1)$$

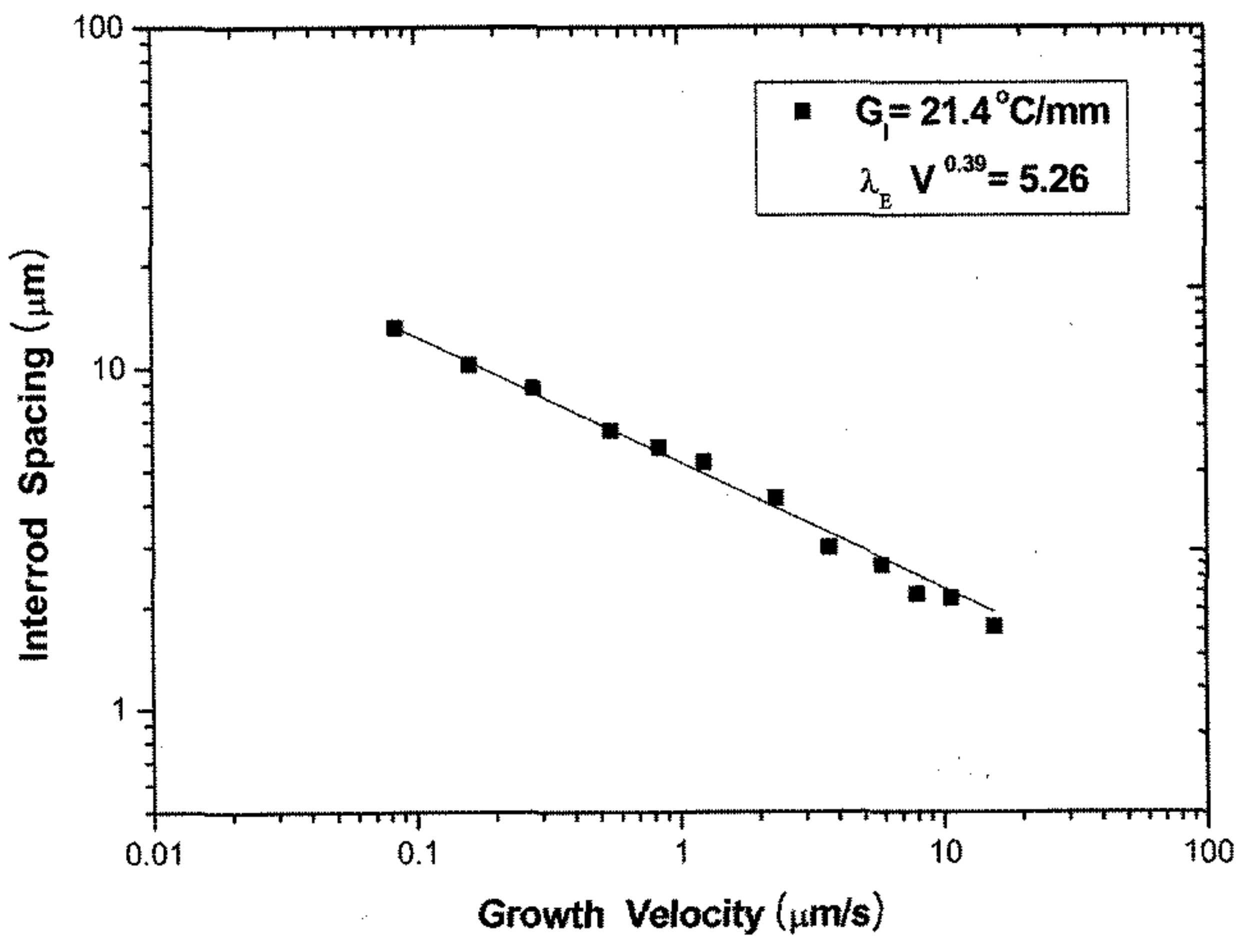

Fig. 3. The plot of interrod spacing, λ_E, as a function of growth velocity, V at temperature gradient of $G_l = 21.4$ °C/mm.

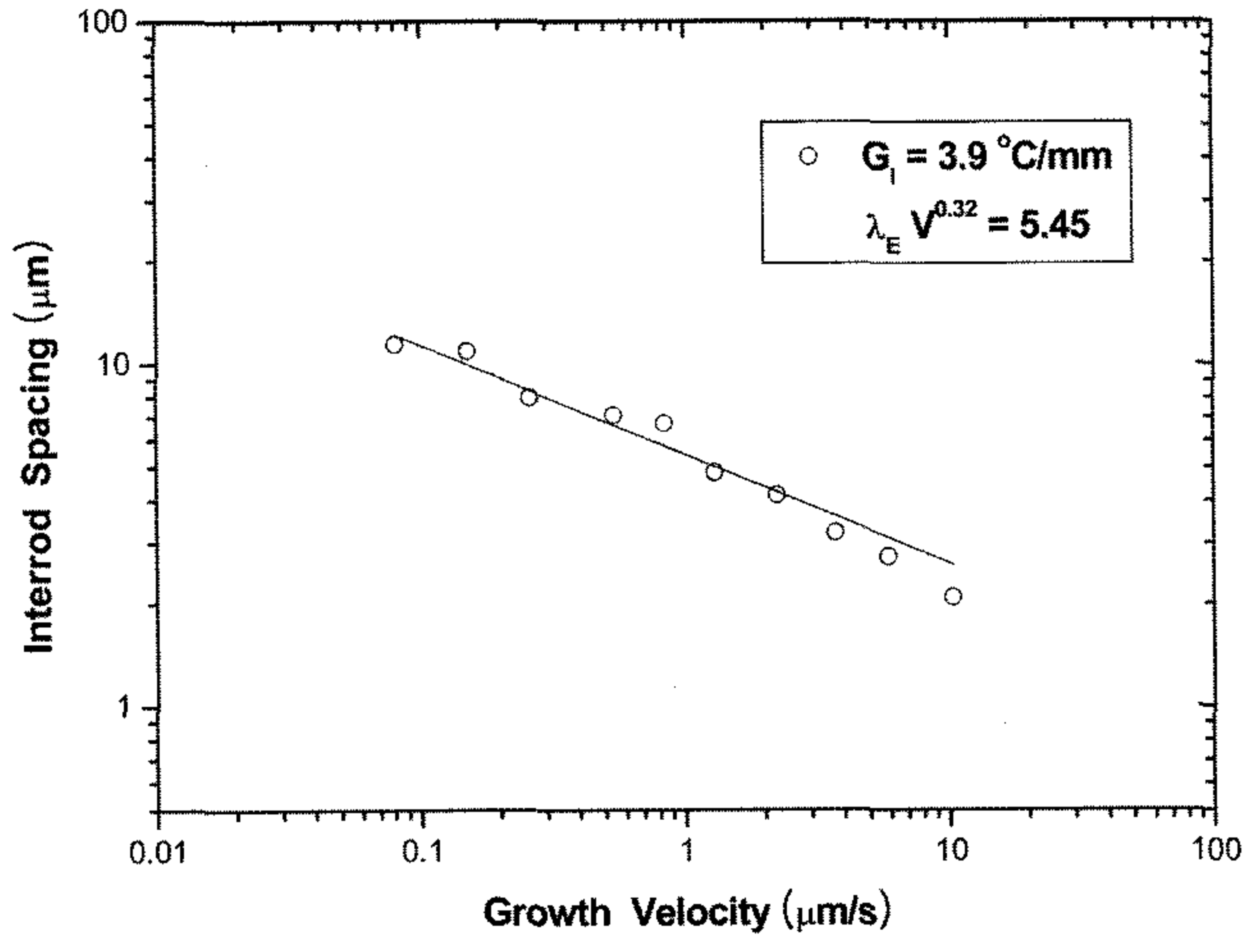

Fig. 4. The plot of interrod spacing, λ_E, as a function of growth velocity, V at temperature gradient of $G_l = 3.9$ °C/mm.

where A is the sectional area and N is the number of rods in that area. Fig. 3 and Fig. 4 are the plots to show the results of interrod spacing, λ_E, as a function of growth velocity, V. As the linear regression analysis was applied to the experimental data, the following fitting equations were obtained for two different temperature gradients respectively;

$$\lambda_E V^{0.39} = 5.26 \text{ for } G_l = 21.4 \text{ °C/mm} \quad (2)$$

$$\lambda_E V^{0.32} = 5.45 \text{ for } G_l = 3.9 \text{ °C/mm} \quad (3)$$

Jackson and Hunt [2] derived a steady-state solution for diffusion equation during the solidification of eutectic alloy and obtained the following relationship of λ_E and V, $\lambda_E V^{0.5} = K$ where K is a constant related to phase diagram and thermodynamic data. Therefore the exponent numbers of growth velocity in this experimental study were smaller than the theoretical value, 0.5, but

Table 1
The variation of interrod spacing with sample rotation rate at growth velocity of 0.55 mm/s and temperature gradient of 21.4 °C/mm

Rotation rate (rpm)	λ_E (μm)
No rotation	7.9622
15 rpm	7.2429
110 rpm	6.8383
220 rpm	7.7428

the numerous experimental investigation showed some deviation of the exponent number of growth velocity to range from 1/3 to 1/2 [6]. Table 1 shows the variation of interrod spacing that decreased slightly as the sample rotation was applied during directional solidification. The similar results were previously published for Sn-0.9 wt%Cu alloy [7]. Also, the refining of the eutectic microstructure in Bi-MnBi rod eutectic system under microgravity was reported and explained as the reduced convection effects [3]. The influence of convection on rod spacing of eutectics was analyzed with a numerical model and the fact that the spacings between the rods increase with an increase in convection, was confirmed by R. Caram *et al.* [8]. Therefore, it is thought that the slight decrease of interrod spacing of $NaNO_3$-4.56 wt%NaCl with sample rotation is due to the reduced convection in front of solid-liquid interface during the solidification.

4. Conclusion

The partial phase diagram of $NaNO_3$-NaCl system was very similar to those of other eutectic metallic systems and the eutectic temperature was determined as 294.5 °C. A typical microstructure of rod eutectics, $NaNO_3$-4.56 wt%NaCl consisted of uniformly spaced NaCl rods in a hexagonal array within $NaNO_3$ matrix. The results of interrod spacing, λ_E, as a function of growth velocity, V, were obtained as $\lambda_E V^{0.39} = 5.26$ ($G_l = 21.4$ °C/mm) and $\lambda_E V^{0.32} = 5.45$ ($G_l = 3.9$ °C/mm) and the exponent numbers of growth velocity in this experimental study were smaller than the theoretical value, 1/2. The sample rotation applied during directional solidification made the interrod spacing to decrease slightly. It is thought that the slight decrease of interred spacing of $NaNO_3$-4.56 wt%NaCl with sample rotation is due to the reduced convection in front of solid-liquid interface during the solidification.

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